

CHEMISTRY

IN

EVERYDAY LIFE

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AUTHORS' PREFACE

In preparing this text the authors have included all necessary descriptive matter; have stated and illustrated all the common laws of elementary chemistry; have included many problems to illustrate the practical applications of chemistry; and have made free use of cross references.

It has seemed best to offer a wide range of material, although it has made a text somewhat larger than the average elementary chemistry.

The college requirements may be met if the student studies the first 393 pages. The selection of the material included in Chapters 25 to 40, inclusive, was based upon reports received from many teachers of chemistry throughout the United States. The selection of material for study from these chapters must be left to the teachers in charge of the classes so that local conditions may be taken into account. It is not intended to have a class cover all of the work in a year.

The authors wish to thank the many firms and individuals who have aided in the preparation of this text either by suggestions or by furnishing material or illustrations, especially The Central Scientific Co., The McIntosh Stereopticon Co. and Mr. W. L. Bentley who have furnished illustrations; several of the boys of the Harrison Technical High School who have made many of the drawings, and the girls in the same school who have aided in the stenographic work.

THE AUTHORS..

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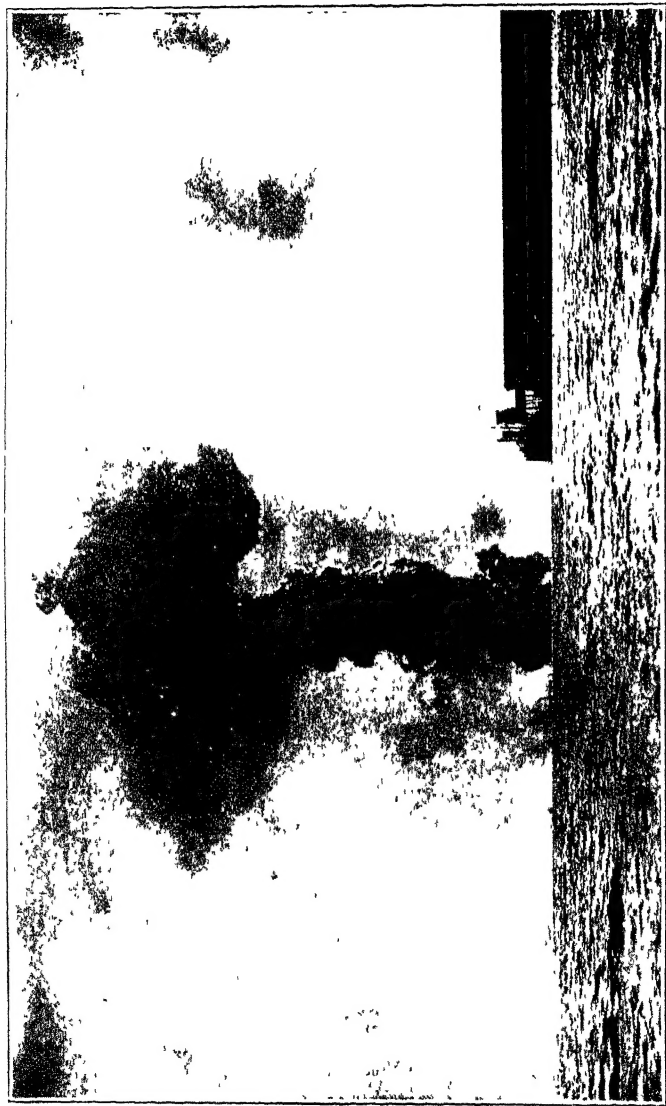
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Frontispiece—Explosion of 600,000 Pounds of Dynamite in Baltimore Harbor

INTRODUCTION

In beginning the study of chemistry, the student may wonder at the large number of facts hitherto unknown to him. Many chemical processes are used daily, but entirely without consciousness on the part of the student. Every breath means chemical changes occurring in the lungs; every bite of food taken goes through that wonderful and mysterious human laboratory consisting of the mouth, stomach and intestines. Only in rare instances, when some antagonistic substance has been taken, does he realize that any changes have occurred.

The clothing may be cotton or wool; or it may be mercerized. Again it may be made of artificial silk. It is usually dyed—sometimes with the natural dyes, but more often with the products of the chemist's art, ever increasing the number of shades to meet the passing fancy.

The houses we inhabit may be of wood or stone, or they may be of concrete. The nails of iron or steel, the mortar to hold together the bricks or stones, the paint to give it a pleasing appearance, the glass in the windows and roofing paper, now widely used, are all subjects for study in the field of chemistry.

The filaments of the electric lights, the gas used to cook our food, the coal used to heat our rooms, the paper used in the books and magazines we read, the money we spend to purchase them, the medicines we take when ill, or the beautifying (?) cosmetics all offer a most interesting opportunity for the student to study along chemical lines, and to apply this knowledge to his advantage.

The importance of chemistry either as a science or in its practical bearings cannot be overestimated. It is the corner stone of medicine, pharmacy, sanitation, agriculture and other sciences. Chemistry is the ruling factor of practically all of the leading industrial plants of the world, and is being regarded with

greater respect by all manufacturers every year. Industrial laboratories are becoming more numerous as manufacturers realize the need of chemical control in order to secure uniformity of products. Where the chemist was formerly looked upon as a needless luxury, he is now considered an absolute necessity in competitive big business, and it is not unusual to find a dozen or more chemists, and in a few instances as many as a hundred chemists employed by a large firm.

During the World War the importance of the chemist was realized more than ever. Chemistry offered very effective weapons against the enemy and while during the first part of the war, as during the twenty or more years immediately before the war, Germany realized the importance of chemistry more than the Allies, this condition did not last. Had either side realized at the beginning the effectiveness of the various gases used at the end of the war, either the war would not have been started, or it would have been over in a few weeks. What will happen in the next great war no one can predict, but it is sufficiently clear that the nation that can make the most effective use of chemistry will have the best chance of winning. This statement is made, not to glorify war, but to show the student that the Nation cannot afford to overlook any opportunity of giving thorough training in chemistry to all who may wish to take up the study in great detail.

Beginning the study of chemistry is similar to beginning the study of a foreign language. You cannot expect to know very much in a year of high school chemistry; but it is possible for every student to grasp some of the fundamental laws and their applications in everyday life. Just as dawn follows darkness so will you gradually see light in your study of this most fascinating subject. When the student once realizes that he cannot avoid chemistry even if he tries; that there is nothing in the material universe that is not a part of chemistry; that the elements of his own body are the same as those found in the earth; and that his body after death will eventually decompose and become part of

other compounds, he will begin to comprehend the vastness of the subject and not become discouraged if he fails to understand everything clearly at the beginning. Diligent study, with questions about the more difficult portions, will work wonders.

CHEMISTRY IN EVERY-DAY LIFE

CHAPTER I

PHYSICAL AND CHEMICAL CHANGES; ELEMENTS AND COMPOUNDS

1. **Matter and Energy.** In the study of chemistry the student will be considering both *matter and energy*. The customary definitions of physics may be taken to explain these terms, but the emphasis in chemistry is upon *matter in its various changes*, rather than upon *matter as a carrier of energy*, as in physics. *Energy plays an important part*, however, in chemistry, either being necessary to *bring about many of the changes in matter*, or being *set free* by the changes that occur.

2. **Relation of Physics to Chemistry.** In spite of the different emphasis in the two studies, *many topics belong equally well to either science*, while others are treated only in physics or only in chemistry. In the following diagram, if the topics

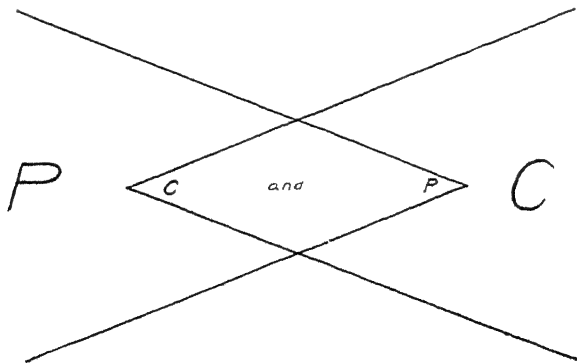


FIG 1 Relation of Chemistry to Physics.

belonging only to chemistry are written in the triangle marked *C*, and those belonging to physics in the triangle *P*, the diamond-shaped portion would contain the topics belonging equally well to both.

Some of the topics belonging to both sciences are gas laws, specific heat, specific gravity, solubility, fusion, vaporization, molecular weight, solidification, electrolysis, etc.

3. Physical States. Matter may be divided into *solids*, *liquids*, and *gases*. In a solid there is usually no tendency to change either shape or volume; in a liquid the volume will remain constant, but the shape will be that of the containing vessel; while in a gas neither volume nor shape will remain constant.

4. Physical Properties. The term "Property" means a distinguishing mark or characteristic, which serves to identify the substance. Physical properties are the common physical characteristics. For example, the chief physical properties of gases are six—color, odor, taste, weight, solubility and liquefaction. In §30 may be found the list of chief physical properties of other substances.

5. Chemical Properties refer to the behavior of the substances, instead of the appearance. For convenience we may group the chemical properties of an element around three heads: (1) its relation to combustion; (2) its action when brought into contact with metals, or electro-positive elements; (3) its action when brought into contact with non-metals, or electro-negative elements or groups. The chief chemical properties of compounds include: (1) its relation to combustion; (2) its action when heated alone; (3) its action when heated with another substance; (4) its action when placed in a solution of another substance; (5) its action when in solution and poured into another solution. See §30.

6. Physical Changes refer to the *changes in the general appearance of a substance which do not alter its composition*. If we heat a piece of ice it turns to water; if we heat the water it

turns to steam; and if the heat is removed, the steam will become water, and the water finally turns back to ice. There has been *no change in the essential nature* of the substance. Many physical changes reverse by a simple reversal of conditions.

7. Chemical Changes refer to *changes in the composition* of the substance, which make it something else, differing in one or more ways from the original substance. If we heat some sugar strongly, we obtain a black substance with a disagreeable odor. Water has been driven out and carbon is left. We cannot, however, recover our original sugar by mixing water with the carbon. Note also the souring of milk; the rusting of iron; etc. A chemical change is not, however, necessarily permanent, since many chemical changes are reversible—that is, they work both ways—and the reversal may sometimes be brought about by a simple reversal of conditions, as when mercuric oxide is only moderately heated until part of the oxygen is driven off and the color has changed from bright red to nearly black. If the heat is removed and the black powder is poured off where it comes in contact with the air, oxygen is taken up readily and the bright red color appears. That we have our original substance may be proven by repeated heatings and coolings, provided we do not heat the oxide strongly enough to drive off all of the oxygen, leaving only mercury, which will remain practically unaltered in the air.

8. Comparison of Physical and Chemical Changes. The following brief table shows the essential differences between physical and chemical changes;

<i>Physical Changes</i>	<i>Chemical Changes</i>
Always accompany chemical changes.	Need not accompany physical changes.
Changes in shape, size or state.	May change shape, size, state, odor or color.

Need not be permanent, but may be.	Need not be permanent, but are so more frequently than in physical changes.
Do not produce change in composition.	Produce change in composition.
Reversal of process often brings back the original substance.	Simple reversal usually does not bring back the original substance, but more elaborate processes may do so.

9. How Can We Tell a Chemical Change? In deciding whether we have a chemical or physical change, the final proof must lie in knowing that we *have a change in composition*, with corresponding changes in the properties. While we may not be able to tell easily in some experiments, there are certain evidences of chemical change, and the probability that the change is chemical increases as the evidence multiplies. (1) There may be a *change in the color*, as when sugar is strongly heated. (2) There may be a *change in state*, from a solid to a liquid or a gas, or vice versa, particularly when two solutions are mixed, or when we pass the electric current through acidulated water, but not when water is heated. (3) All chemical changes involve a *change in the temperature*, but there may be change in the temperature without producing a chemical change. Thus if magnesium ribbon is held in the Bunsen flame the ribbon burns to magnesium oxide, but a piece of glass does not burn. (4) *Changes of odor* indicate a chemical change, as when we rub some ammonium chloride and slaked lime with our hands. (5) If other properties change, giving *evidence of a change in composition*, it is good evidence of a chemical change, but for a beginner an absolute knowledge of changes of composition is impossible, so that he must rely more upon the changes in physical properties to guide his judgment.

10. Things To Watch. In determining whether we have a chemical change, and to tell what kind of change we have brought about, we must watch carefully the following points:

- (1) We must know the *properties of the factors* or *what we use*.
- (2) We must *study carefully all that occurs* during the progress of the experiment.
- (3) We must remember that no matter what *we do, we can never create nor destroy matter* however much we may change its form and appearance.
- (4) We must know the *properties of the products*, or *what we obtain*, and *compare them with the original properties*.

11. Physical Division. It is often necessary to divide a substance into very fine particles in order to obtain the best results in a chemical experiment. Physical division is accomplished in one or more of four methods—we may *cut* a substance with a knife; *crush* it; *grind* it in a mortar; or we may *dissolve* it in water or some other substance. (See Chapter 5.) These methods leave the substance as it was originally, except that in the solution of certain substances in water, the very small particles probably are separated into what are known as *ions*, or electrically charged atoms. (See §101, ff.) However, it is usually possible to evaporate the water from a solution and to obtain the original substance.

12. Limits of Division by Solution. When we have dissolved some sugar in water, we find that if properly mixed, all parts are equally sweet, which leads to the conclusion that the sugar is equally distributed throughout the solution.

If we use some of the aniline dyes we find that it is possible to add water to the solution until by weight we have only one part of the dye to several million parts of water, but the color is still visible. The color will gradually become weaker and weaker until it finally disappears entirely. What was the condition of the dissolved sugar or dye? We say, for want of a better explanation, that the division has been carried to the point of obtaining the *molecules* of the substance, the word meaning “a small body.”

13. Chemical Division. By adopting suitable methods we may break up a substance chemically. It will then no longer

act as it did in the beginning of our experiment but will exhibit properties that are in general very much different. Common salt is made up of two substances, sodium and chlorine, chemically combined, and the salt will dissolve quietly in water. Sodium, however, acts very differently from salt when placed in water. The sodium will spin around and eventually disappear and may exhibit a flash of flame, caused by the combustion of some of the hydrogen which the sodium liberates from the water. The other part of the salt, chlorine, is a greenish yellow gas of a very disagreeable odor, dangerous to breathe, just as the sodium and water combination would be dangerous to drink. How different from the common salt which everyone desires each day!

14. Methods of Chemical Division. There are four methods of dividing a substance chemically:

(1) *By heat.* If we heat some potassium chlorate it will be broken up into oxygen and potassium chloride.

(2) *By a chemical reagent.* Very often when one chemical substance is added to another, particularly when the substances have been previously dissolved in water, the two substances will each be broken up and a new combination will occur, producing usually two or more substances differing from the original material used, but containing all of the constituent parts of the original. Thus, when a solution of silver nitrate is added to a solution of common salt we obtain a white curdy precipitate of silver chloride in a solution of sodium nitrate.

(3) *By the electric current.* Many substances *in solution*, and sometimes when fused, yield their constituent parts when the electric current is passed through them. Thus, acidulated water (i.e. dilute sulphuric acid) will yield hydrogen and oxygen. In the same manner, using carbon electrodes, *hydrochloric* acid will yield hydrogen and chlorine.

(4) *By light.* Light much less frequently plays the part of breaking up a chemical compound, but is sometimes very active towards chemical substances. The process of making a photo-

graph is due largely to the action of light upon the materials used.

15. Limits of Chemical Division. When we have reached the limits of chemical division we have divided the molecule into its parts and have reached what Dalton called the *atom*. We shall see a little later that the present theory of chemistry carries the division still farther, but we shall not yet enter into a discussion of the theory. When a substance is divided into the atoms it usually takes on different characteristics, one of which is the *tendency to combine*.

16. Combination of Atoms. When two or more atoms of the same kind unite they form what is called a *simple molecule containing only one kind of matter*. When two or more atoms of different kinds unite they form what is called a *compound molecule*. As an example of the formation of simple molecules, the atoms of hydrogen liberated in the electrolysis of dilute sulphuric acid, combine to form molecules of hydrogen. This kind of action occurs when there is nothing else present with which the hydrogen can react. If the hydrogen liberated in the atomic condition comes in contact with many substances, however, it will react with them forming compound molecules. Hydrogen thus acting in the *atomic or ionic condition* is often called *nascent hydrogen*, or hydrogen *just being born*, and is much more active than a stream of hydrogen from the generator.

17. What holds the atoms together? In some respects the force holding the atoms together resembles cohesion, particularly in the case of simple molecules, but with compound molecules the force seems to correspond more nearly to magnetism. Like any other force it may be either strong or weak; but if it is to act at all the atoms must be separated by only very small distances. This force may be helped by heat, light, electricity or reagents in many cases, but on the other hand there are instances where these agencies act as a hindrance rather than as a help.

18. Classification of Chemical Substances. Chemical substances are either *compounds* or *elements*. When the elements

join chemically they form a *chemical compound*. When chemical compounds or elements are *simply mixed together without chemical combination they form a mechanical mixture*. Thus gold, silver, lead, copper, etc., are elements, salt, sugar, borax, or soda are chemical compounds; but if they were all mixed together without chemical union they would form a mechanical mixture.

19. The Old Ideas of Elements. For many years the term element was taken to mean "something to which all other substances may be reduced," and different thinkers, without trying to investigate the subject experimentally, chose different common things as "primal matter" water, air, earth and fire being the ones usually chosen.

20. The Present Idea of an Element is, *that the substance can not be divided into two or more simpler substances*, and the attempt to reduce all substances to *any one material substance* has long been abandoned; moreover, it appears that the number of elements is increasing rather than decreasing. The list of elements is changed to some extent from time to time as new substances are classed as elements. The peculiar behavior of radium has led to a different theory known as the electron theory which is, in brief, that all substances consist of electrical charges, the number and grouping of the charges determining the nature of the "element." This theory will be explained more in detail in connection with the discussion of radium, Chapter 23.

21. The Common Elements. A list of the common elements with which the student is expected to become familiar is given at this time, together with some of the common elemental constants that are used in the study of chemistry. The student is expected to memorize the symbol, valence and atomic weight of carbon, chlorine, copper, hydrogen, iron, nitrogen, oxygen, potassium, sodium, sulphur and zinc at this time in order to be able to work simple problems and equations as soon as possible without having to refer to the table. The others may be learned as studied in the text.

LIST OF COMMON ELEMENTS

<i>Element</i>	<i>Symbol</i>	<i>Ordinary Valence</i>	<i>Approximate Atomic Weight</i>
Aluminum	Al	3	27
ANTIMONY (Stibium)	Sb	3	120
ARSENIC	As	3	75
Barium	Ba	2	137
Bismuth	Bi	3	208
BORON	B	3	11
<u>BROMINE</u>	Br	1	80
<u>Cadmium</u>	Cd	2	112.5
Calcium	Ca	2	40
CARBON	C	4	12
*CHLORINE	Cl	1	35.5
Chromium	Cr	2, 3 or 6	52
Cobalt	Co	2	59
Copper (Cuprum)	Cu	1 or 2	63.5
*FLUORINE	F	1	19
Gold (Aurum)	Au	1 or 3	197
*HYDROGEN	H	1	1
IODINE	I	1	127
Iron (Ferrum)	Fe	2 or 3	56
Lead (Plumbum)	Pb	2	207
Lithium	Li	1	7
Magnesium	Mg	2	24
Manganese	Mn	2, 4 or 7	55
<u>Mercury (Hydrargyrum)</u>	Hg	1 or 2	200
Nickel	Ni	2 or 3	58.5
NITROGEN	N	3 or 5	14
OXYGEN	O	2	16
PHOSPHORUS	P	3 or 5	31
Platinum	Pt	4	195
Potassium (Kalium)	K	1	39
SILICON	Si	4	28
Silver (Argentum)	Ag	1	108
Sodium (Natrium)	Na	1	23
Strontium	Sr	2	87.5
SULPHUR	S	2, 4 or 6	32
Tin (Stannum)	Sn	2 or 4	119
Zinc	Zn	2	65

In order to enable the student to see at a glance certain properties of the elements, the names of the *metallic elements* are printed in ordinary type, as Aluminum, while the names of the *non-metallic elements* are printed in small capitals, as ARSENIC. Latin names are given in parentheses. Liquids are underscored; gases are marked with an *; the others are solids. A complete list of the elements, with their symbols, valences and atomic weights, may be found on the back cover page. The *symbol* is the abbreviation for an element used in writing formulas and equations—a sort of *chemical shorthand*. The *valence* means the *combining power*, more fully explained in Chapter 9. The atomic weight means the relative weight as compared with oxygen (16) or with hydrogen (1). Since the real ratio of oxygen to hydrogen is 15.879 instead of 16 the atomic weights differ somewhat in the table given on the back cover page. In the adjoining table the *approximate weights* are given and the student should use these in all of his computations unless more exact weights are called for.

Of these 37 elements 14 are non-metals and 23 are metals. At ordinary temperatures 5 are gases, 2 are liquids, and 30 are solids.

22. The Abundance of the Elements. In his work entitled "Data of Geochemistry," Prof. F. W. Clarke, Chief Chemist of the United States Geological Survey, gives the following data concerning the relative abundance of the elements:

The specific gravity of the crust of the earth for the first 10 miles is not less than 2.5 and not more than 2.7.

By weight the total material is divided into three parts

	Between	and
Atmosphere	0.03	0.03
Oceans (hydrosphere)	7.08	6.58
Crust (lithosphere)	92.89	93.39
	<hr/>	<hr/>
	100.00	100.00

The relative percentages of the elements are given as follows:

<i>Element</i>	<i>Lithosphere</i>	<i>Hydrosphere</i>	<i>Average with Atmosphere</i>
Oxygen	47.33	85.79	50.02
Silicon	27.74	—	25.80
Aluminum	7.85	—	7.30
Iron	4.50	—	4.18
Calcium	3.47	0.05	3.22
Magnesium	2.24	0.14	2.08
Sodium	2.46	1.14	2.36
Potassium	2.46	0.04	2.28
Hydrogen	0.22	10.67	0.95
Titanium	0.46	—	0.43
Carbon	0.19	0.002	0.18
Chlorine	0.06	2.07	0.20
Bromine	—	0.08	—
Phosphorus	0.12	—	0.11
Sulphur	0.12	0.09	0.11
Barium	0.08	—	0.08
Manganese	0.08	—	0.08
Strontium	0.02	—	0.02
Nitrogen	—	—	0.03
Fluorine	0.10	—	0.10
All others	0.50	—	0.47
Total			100.00

From this it may be seen that the eight most abundant elements constitute more than 97% by weight of all materials that make up the earth. (See Fig. 2.)

Of the 83 elements now recognized, less than one-half are common, and not more than one-fourth are necessary for civilized life.

The estimation for the composition of the oceanic salts may be found in §118.

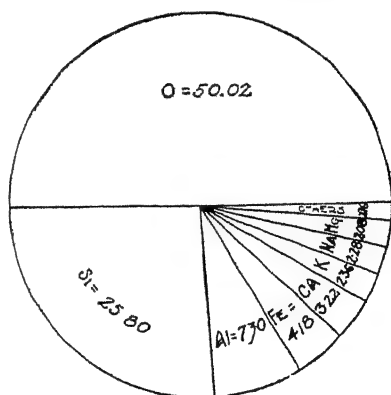


FIG. 2 Percentage of the Elements.

Alchemical Signs

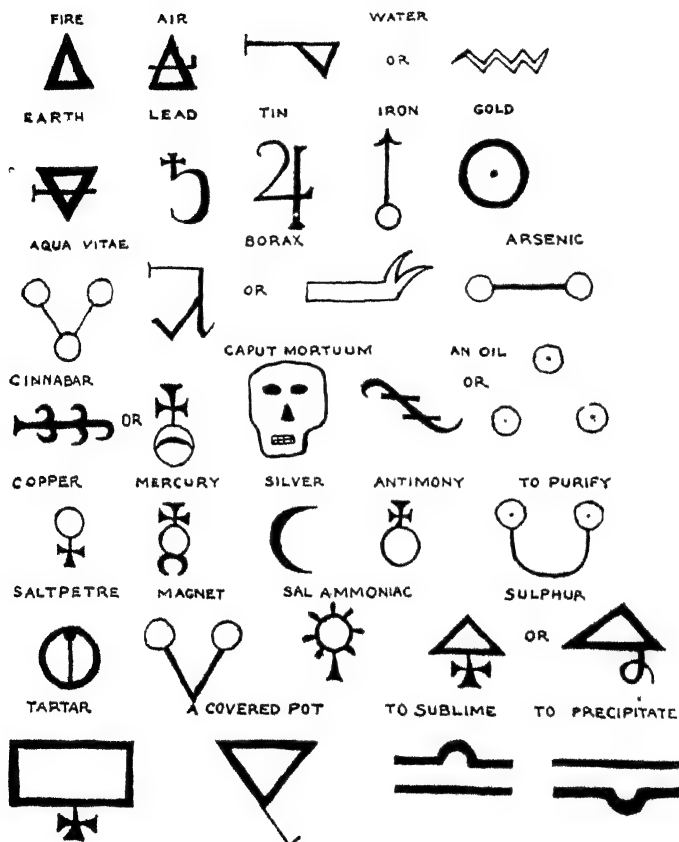


FIG. 3. Alchemical Signs and Symbols.

During the Middle Ages when little chemistry was known the alchemists used various signs and symbols for elements, compounds and processes that cannot be read without a key. (See Figs. 3 and 4.)

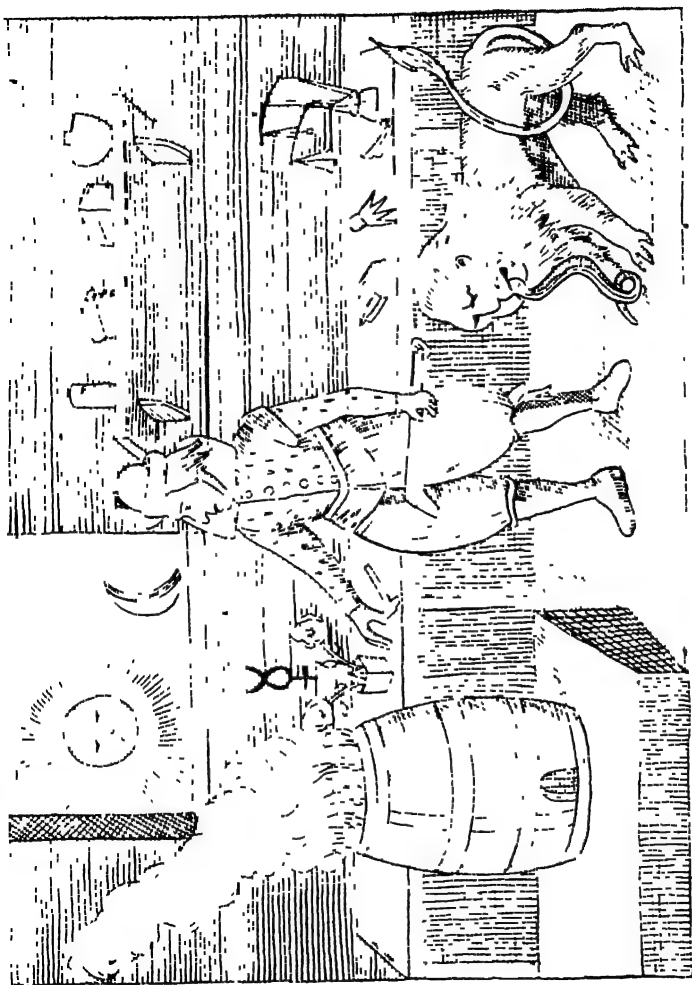


FIG. 4. Alchemical Representation of Processes.

23. Classification of Chemical Compounds. Chemical compounds are usually divided into two large groups; the first consisting of those *not containing carbon*; the second those *that do contain carbon*. It has long been customary to call the carbon compounds organic, from the old belief that they must be derived from living organisms, but this theory has long been abandoned. The logical name, therefore, for the non-carbon compounds was *inorganic compounds*. Elementary chemistry deals largely with the non-carbon compounds.

24. Formation of Compounds. Elements unite to form compounds. Sometimes only two elements are found in a compound, as when sodium combines with chlorine to form common salt, called in chemistry sodium chloride. At other times non-metallic elements unite to form what is called a radical. A radical usually passes from one compound to another without changing its form. The student should familiarize himself with radicals as soon as possible. A list of the more common radicals is given in §155. The student should learn at this time the following radicals: NH_4 , NO_3 , $\text{C}_2\text{H}_3\text{O}_2$, OH , SO_4 , and CO_3 . If he thoroughly masters these six at this time he will have no difficulty in understanding all of the common illustrations given, and his work will be much lighter. He should also remember where the list is found and refer to it as necessary. In applying his knowledge of radicals the student should combine the ammonium radical with the others and then write combinations of the other common metals with the same acid radicals. He should accustom himself to think of the compounds in terms of the radicals from the first. He should think of the valence of the radical as well as the valence of the metal combined with the radical. Only in this way can he make rapid progress.

25. Classification of the Non-Carbon, or Inorganic, Compounds. In accordance with their chemical behavior the non-carbon compounds are nearly all included in the following divisions:

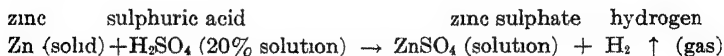
(1) *Acids*. These are generally sour and consist of hydrogen in combination with a radical. They generally turn litmus and other vegetable colors red or pink, and have no effect upon phenolphthalein, unless it has been colored red by an alkali. The acid then removes the red color. Common examples are nitric, hydrochloric and sulphuric acids.

(2) *Bases*. These are the opposites of the acids. Their taste is burning or bitter. Their action upon litmus is to turn it blue; other vegetable colors are turned blue or green; while phenolphthalein in the presence of a base turns magenta red. Examples are sodium hydroxide, potassium hydroxide and ammonium hydroxide.

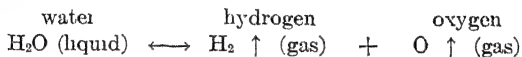
(3) *Salts*. Whenever an acid and a base are brought together they react to form *water and a salt*, the name depending upon the acid and base used. Salts may be formed in several other ways, but for convenience they may be considered as the product resulting from the action of a base upon an acid. Examples are sodium nitrate, potassium sulphate, ammonium oxalate.

Acids, bases and salts will be discussed more fully in Chapter 8, but it is necessary for the student to begin to group his ideas around this central point, and to identify the common chemical substances as one of these three whenever possible.

26. Reactions and Equations. Whenever chemical action occurs we have what is known as a *reaction*, and the result may be written in a *concise form known as an equation*; a shorthand statement of what has occurred. The *substances put together to produce the reaction are known as factors* (doers); the *substances formed are known as products*. The separation of the factors from the products in an equation is indicated by an arrow, the head pointing to the products.



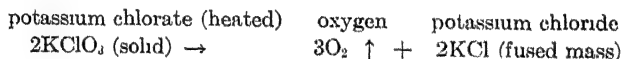
This should be read in this manner: Zinc and dilute sulphuric acid will produce zinc sulphate and hydrogen. Later the student will learn how to read an equation more fully. When the arrow points in both directions it indicates that the reaction may proceed in either direction, as



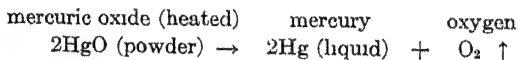
In any case the number of atoms of each element must be the same on both sides of the arrow. When the arrow points upward after an element or compound, it indicates that a gas is given off. When it points downward it indicates a precipitate. Other products are usually solutions, but may be liquids not containing a dissolved substance.

27. Kinds of Common Reactions. There are four kinds of common reactions in elementary chemistry. These are:

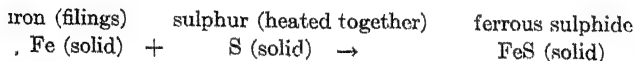
(1) *Analysis or decomposition*, where a single substance is separated into elements or groups. Thus when potassium chlorate is heated



Reduction, or the loss of oxygen or other electro-negative element thus increasing the relative amount of the electro-positive element is one form of analysis.



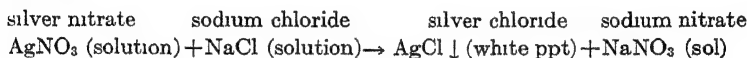
(2) *Synthesis* is where two or more elements unite to form a single compound:



Oxidation, or the decrease in the percentage of the electro-positive element is one form of synthesis. Reverse the equation given for reduction beginning with oxygen.

(3) *Substitution.* When one element in a compound is *replaced by another* it is known as substitution; the replaced element is set free, at least temporarily. Many times a gas is given off which will escape into the air or into a special receiver. Thus zinc will replace the hydrogen of dilute sulphuric or hydrochloric acid and set the hydrogen free. (See §26.) It is frequently stated that the zinc dissolves in the acid, but this is not strictly true for there is a chemical reaction between the two substances and we cannot get our zinc back again in the original form by evaporation, which we can do in a true solution. (See Chapter 5.)

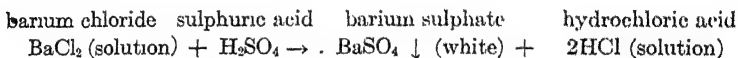
(4) *Metathesis or Double Decomposition.* When two solutions are mixed, there is very frequently a *double decomposition* and a recombination in a different manner. *The metallic elements may be said to have changed places.* If a solution of silver nitrate is mixed with a solution of sodium chloride, (common salt) the sodium of the salt exchanges places with the silver of the silver nitrate, forming silver chloride and sodium nitrate. All of the original material is still there, but it is arranged in a different manner.



Usually the water in the solution does not take part in the reaction, but if it does it is called hydrolysis.

28. Tests. Often during the course of an experiment a substance is obtained whose identity is not perfectly clear, or we may wish to verify our reasoning or belief that we have a certain compound. It is then necessary to apply what is known as a test. Certain acids, bases and salts in solution give us the common reagents used in testing. These may be added in small portions to some of the solution of the substance we are trying to identify, and the results obtained are compared with known results obtained when some of the same reagent is added to a solution of a known compound. Thus a test for sulphuric

acid or soluble sulphates is to add a few drops of barium chloride solution to the solution we wish to test. A white precipitate, insoluble in water, alkalies or common acids, except concentrated sulphuric acid, indicates the presence of barium sulphate, thus showing the presence of the SO_4 group in the original solution, the barium sulphate being formed by metathesis, as in the equation



It is often necessary to apply more than one test to confirm results. The systematic testing of a substance to learn which substances it contains is qualitative analysis. If we learn how much of each substance is present it is quantitative analysis. Proximate analysis states the results as water, carbon dioxide, volatile matter, ash, etc.; ultimate analysis states the results as hydrogen, oxygen, nitrogen, sulphur, etc.

29. Importance of Chemistry. That chemistry ranks as a science may be seen from the fact that *it can predict results when the conditions are known*. Chemistry is more than a mere accumulation of facts. It is essentially *a collection of related facts where the relations are known*. Its laws may in many cases be proven by direct experiment, and where the student cannot prove absolutely it will be found that the statement of chemical law and theory will interpret the results we are led to expect. Some of the facts bearing upon the importance of chemistry were touched upon in the introduction, so that the student might grasp the significance of the study and the magnitude of the field. It may safely be said that if everything pertaining to chemistry could be destroyed nothing would remain. As an illustration of the importance of chemistry it is not at all uncommon for the dressed meat from an ox to be sold for less than the animal cost alive. How can the packing houses afford to do it? They are not in the business of supplying meat as a charitable organization, but by the development of by-products from the

parts an ordinary butcher would throw away they are enabled to sell meat at a price far below what it would cost if only the meat were sold. The natural growth of the packing houses may be seen from the following brief statement of the nature of the by-products from cattle, sheep and hogs.

Hair is used for making curled hair for stuffing mattresses, for upholstering furniture, as a substitute for camel's hair in making paint brushes, while the coarser varieties are used for plaster retarder, and for making hair felt.

Wool is used for making clothing, felt hats, carpets, rugs, and other finished articles.

From the hard portions of the horns, hoofs and bones are manufactured hair pins, buttons, combs, crochet hooks, tooth brush handles, knife handles, umbrella handles, chess men, dice, letter openers, napkin rings, and many other articles. From the softer portions are made, glue, gelatine, neatsfoot oil, bone meal for fertilizers, while further allied with these products are sand paper, emery paper, garnet paper and crystolon paper, where the abrasive material is held on with glue.

The hides are used for making leather of various kinds. The fats are boiled with alkalies to make soaps, which may contain glycerine, or the latter may be recovered as a separate product, or to be used in explosives.

Rennet powder is the curdling ferment of the calf's stomach, and among other powders obtained in the meat industry are peptone, pepsin, thyroid powder, ox gall and pancreatin.

Sheep intestines are used to make tennis strings, music strings, and surgical ligatures.

Blood is used in making certain kinds of sausage; or it may be used as a fertilizer, the same as tankage, which is made from the trimmings and scraps.

Oleostearin is a high grade neutral tallow used for candies, chewing gum, etc., while ordinary tallow, used in soaps; tallow oil used in compound lubricants; lard oil used as illuminating

oil in light houses, locomotive head lights, etc., are some of the other by-products of the packing house industry.

Some of the other industries are not so highly organized; but the time will come when every industry that hopes to survive will adopt the motto of the packing houses—"Nothing wasted."

The really practical chemist today must know more than merely how to mix things together from directions. He must know the laws and theories of chemistry, so that when things go wrong he may be able to find and remedy the difficulty; he must be able to secure uniformity of products; he must be able to think out new methods of production without too elaborate experimentation which is expensive in time and money.

A section of a modern industrial laboratory is shown in Fig. 5.

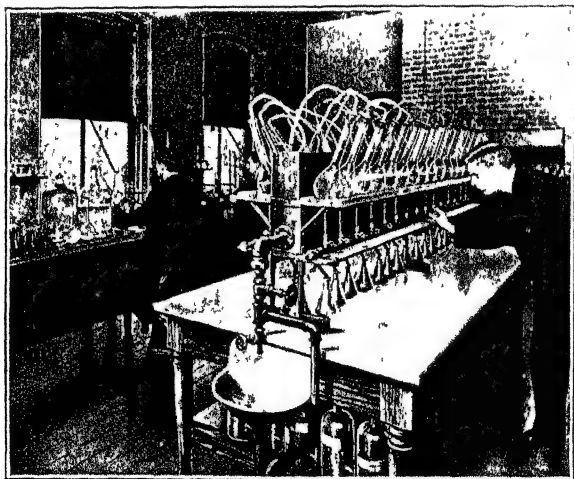


FIG. 5. Part of a Modern Laboratory, Swift & Co.,
Chicago.

30. How to Study Chemistry. In the study of chemistry the student will find that he can make much more rapid progress if he will endeavor to group his ideas around certain important

points and follow a regular outline of study. In the following outline, which has been used very successfully, more topics have been included than will apply to every substance studied. If, for example, the substance is a gas such as oxygen, the first element studied, the student should learn the six common physical properties and not attempt to apply the properties of liquids or solids. In the same manner he should not attempt to apply the chemical properties of compounds to oxygen, since oxygen is an element, and so on.

OUTLINE FOR STUDY

Learn how to use the index. There are 2500 references to the main topics. Consult the tables in the back of the book regularly.

I. Occurrence.

1. *Free*. If so, where, relative abundance, etc.
2. *Combined*. If so, with which elements or compounds, abundance, etc.
3. *Chief sources of supply*, location, etc.

II. Preparation.

1. *If free*, does it need to be separated from other elements or compounds mixed with it?
2. *If combined*, how would you separate it from its combinations?
3. Can you give *any other common method of preparation*?
4. Why would you use the *method* given and the *compound* chosen?
5. How would you *purify* the substance as prepared by your method?

III. Physical Properties.

1. The substance is a gas—Color, odor, taste, weight of a liter, solubility in water, liquefaction, any other special property.

2. The substance is a liquid—Color, odor, taste, solubility, specific gravity, boiling point, solidification point, any other special property. •
3. The substance is a non-metallic solid—Color, odor, taste, solubility, specific gravity, shape of crystals, result when exposed to the air, any other special property.
4. The substance is a metallic solid—Color, luster, melting point, vaporization point, conductivity of heat and electricity, malleability, tenacity, breaking strength, hardness, specific gravity, any other special property.

IV. Chemical properties.

1. Relation to combustion—Does it burn in the air? In other gases? Does it support the combustion of common materials? Of special substances?
2. Combination with other substances.
 - (a) The substance is an element—Does it combine with any of the metals? non-metals? Does it make the combinations by direct or indirect method? Does it react with any compounds?
 - (b) The substance is a compound—What is the effect of heating? Does this reverse when cooled? What is the effect when heated with other selected substances? What are the chief reactions when in solution and mixed with other solutions? Does it react with substances not in solution? How does it ionize? How is it electrolyzed? Secondary reactions? Equations? (Some of these questions will not apply to certain compounds.)

V. Uses. In the laboratory; in daily life; in commerce.

The text will follow the outline very closely. The student should consult the outline constantly and see whether he can

answer the questions as applied to the substance he is studying. For this reason no lists of questions will be given at the end of the different chapters. Although the odor and taste are important physical properties, the student should be careful about smelling unknown substances, and should NEVER TASTE CHEMICALS unless so directed by the instructor.

31. The Metric System is used exclusively in all scientific work. The more important tables for chemistry are the following:

<i>Length</i>	<i>Mass</i>	<i>Capacity</i>	<i>Length</i>	<i>Mass</i>	<i>Capacity</i>
10 millimeters,	—grams or	—liters make 1 centimeter,	—gram or	—liter	
10 centimeters,	—grams or	—liters make 1 decimeter,	—gram or	—liter	
10 decimeters,	—grams or	—liters make 1 meter,	gram or	liter	
10 meters,	grams or	liters make 1 Dekameter,	—gram or	—liter	
10 Dekameters,	—grams or	—liters make 1 Hectometer,	—gram or	—liter	
10 Hectometers,	—grams or	—liters make 1 Kilometer,	—gram or	—liter	

In this table the units are the *meter*, the *gram* and the *liter*. Under ordinary circumstances the only one larger than the units that finds practical use is the Kilogram. The prefixes have the following meanings:

<i>Prefix</i>	<i>Meaning</i>	<i>Abbreviated</i>
milli	thousandth	m.
centi	hundredth	c.
deci	tenth	d.
Deka	10	D.
Hecto	100	H.
Kilo	1000	K.

The units are abbreviated as follows: Meter m; gram g; liter l. One letter used alone refers to the unit. If two letters are used the first refers to the prefix. Cubic centimeter is usually abbreviated cc.

TABLE OF ENGLISH AND METRIC EQUIVALENTS

MEASURES OF LENGTH

- 1 inch = 25.4001 mm. = 2.54001 cm.
 1 foot = 0.304801 m. = 30.4801 cm.
 1 cubic inch = 16.387 cc.
 1 meter = 39.3700 in. = 1.093611 yd.
 1 cm. = 0.3937 in.

MEASURES OF WEIGHT

- 1 oz. Av. = 28.3495 g.
 1 lb. Av. = 453.59 g = 0.45359 kg
 1 oz. Troy = 31.10348 g.
 1 grain = 64.7989 mg. = 0.0647989 g
 1 kg. = 2.2046 lb. Av. = 35.2736 oz. Av. = 32.1507 oz. Troy = 15432.36 grains
 1 g = 0.03527 oz. Av. = 0.03215 oz. Troy = 15.43236 grains.

MEASURES OF CAPACITY

- 1 liquid qt. = 946.33 cc = 0.94633 l.
 1 fl. oz. = 29.57 cc.
 1 fl. oz. Apoth. = 28.4123 cc.
 1 l. = 1.0567 qt. (liquid).

32. Problems. Thermometer changes.

(1) *To Change Fahrenheit to Centigrade*—Subtract 32 from the F. reading; multiply by 5, then divide by 9. $C = 5/9 (F - 32)$.

(2) *To Change Centigrade to Fahrenheit*—Multiply the C. reading by 9; divide by 5; then add 32. $F = 9/5 C + 32$.

The following table shows that these two methods are opposites:

F to C		
read down		
subtract	32	add
multiply by	5	divide by
divide by	9	multiply by
		read up
		C to F

(3) *To Change Centigrade to Absolute*: Add 273° to the C. reading.

(4) *To Change Absolute to Centigrade*: Subtract 273° from the A. reading.

The abbreviations used are Centigrade = C; Fahrenheit = F; Absolute = A. The temperature on the absolute scale is T; on the Centigrade scale is t . Change of temperature is indicated by T' and t' .

Figure 6 shows the comparison of the temperature scales. ALL TEMPERATURES GIVEN IN THIS BOOK ARE CENTIGRADE UNLESS OTHERWISE STATED. The student should invariably use the metric system and decimal fractions unless otherwise directed. All decimal results should be carried to two places.

Success in working the following problems depends upon ability to use positive and negative numbers.

1. Change the following F. readings to C. 4000° ; 259° ; 10° ; -10° ; 32° ; 0° ; 70° ; -80° ; -459.4° .

2. Change the following C. readings to F. 100° ; 212° ; 1050° ; 0° ; 10° ; -10° ; -273° ; -191° .

3. Change all the readings of problems 1 and 2 to the absolute scale.

4. Change the following absolute readings first to C then to F: 10° ; 27° ; 85° ; 273° ; 400° .

5. At what temperature are the readings on the C. and F. scales identical?

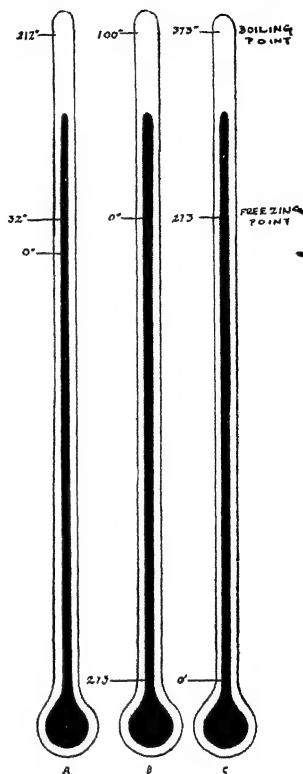


FIG 6 Comparison of Thermometer Scales.

CHAPTER II

OXYGEN

SYMBOL, O; VALENCE, 2; ATOMIC WEIGHT, 16

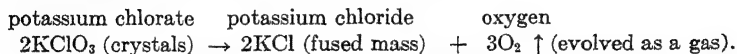
33. Occurrence. Oxygen occurs both *free and combined*. Free oxygen forms about $1/5$ of the atmosphere. Combined oxygen forms about $1/2$ of the earth's crust, $8/9$ of water by weight, and is found in nearly all animal and vegetable substances. It has been estimated that the atmosphere contains fully 1,250,000,000 tons of oxygen, or enough to last for 1,000,000 years without renewal.

34. Preparation. The methods of preparing oxygen depend upon whether we wish (1) *to separate it from the other gases of the air*, where it exists uncombined; or (2) *to obtain it from compounds*. The separation of oxygen from the air is not suitable for the small laboratory, but it is used in large industrial plants manufacturing oxygen for commercial purposes.

In the preparation of oxygen in the laboratory the compound selected for decomposition should (1) be abundant; (2) be reasonably cheap; (3) contain a high percentage of oxygen; (4) decompose without an excessive amount of heat; (5) not yield other contaminating gases. (These general principles apply to the preparation of any substance, modified as necessary.) In the laboratory, methods of obtaining oxygen by the use of heat are most frequently employed, but other methods using light, electricity or chemical reagents are sometimes used. These will be spoken of in order.

35. Methods Using Heat. The best and cheapest method for the beginner is to heat to about 250° equal amounts of potassium chlorate and manganese dioxide, well mixed, in a vessel fitted with stopper and delivery tube. (See Fig. 7.)

Oxygen will be evolved if we heat the potassium chlorate alone, but it must be heated to about 450° . The final equation for the reaction in either case is written



At the temperature required for the mixture, the manganese dioxide does not evolve oxygen, but acts as a *catalytic*, or *con-*
tact, agent serving to bring about the decomposition of the potassium chlorate at a lower temperature than when it is heated alone. In general a catalytic agent brings about the reaction more easily, and is apparently not changed in the course of the reaction, but very frequently it undergoes a series of changes, and ends by appearing in the same form as when it was first mixed with the other substance. If the manganese dioxide is heated alone to about 600° it will give off $1/3$ of its oxygen

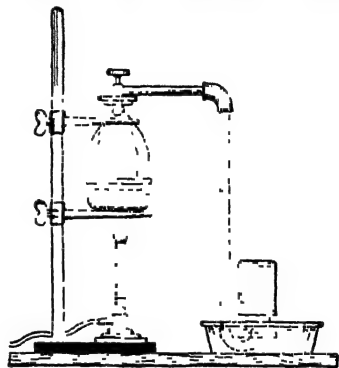
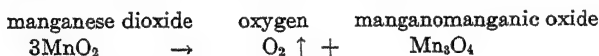


FIG. 7. Preparation of Oxygen from Potassium Chlorate.



36. Certain Oxides of Metals will give off oxygen when heated. The oxides that are sometimes used are limited in number and consist of those *where the force holding the metal and the oxygen together is small*. The adjoining table shows the relative activity of the common metallic substances, the most active standing first. (Hydrogen is included because it acts chemically as a metal; arsenic and antimony act at times as metals.)

Potassium	The metals standing at the head of the list,
Sodium	potassium, sodium, etc., are very active chemi-
Barium	cally and combine vigorously with oxygen, so that
Strontium	they are never found free in nature, and when set
Calcium	free from their compounds they must be kept
Magnesium	under a liquid <i>free from oxygen</i> , such as kerosene,
Aluminum	naphtha, etc. If the metals are exposed to the
Manganese	air they <i>combine at once with oxygen</i> , and the oxides
Zinc	are difficult to decompose even at high tempera-
Cadmium	tures. On the other hand, the metals that stand
Iron	lower in the list do not combine so readily with
Cobalt	oxygen, and may be kept in the air. It is difficult
Nickel	to cause the metals lowest in the list to combine
Tin	with oxygen and when the combination is brought
Lead	about the compounds may be decomposed again
Hydrogen	at only moderate temperatures.

37. Limits of Choice.

Even at the lower end of the list we are limited in our choice, since gold, platinum and silver do not form oxides readily, and are too expensive to use, so that practically the best oxide for this purpose is mercuric oxide, since those above mercury, either require too high a temperature or have other objectionable features. (See Fig. 8.) Mercuric oxide is,

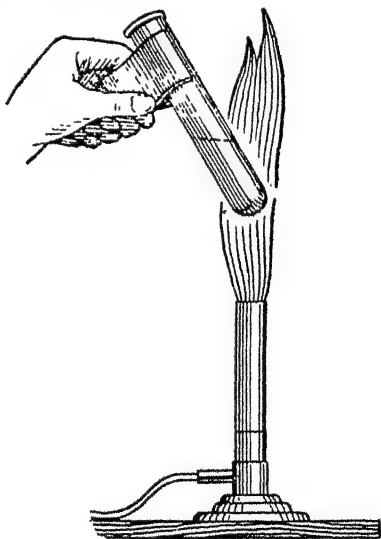
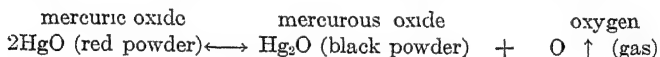


FIG. 8. Preparation of Oxygen from Mercuric Oxide.

however, too expensive to use regularly in the laboratory, and the proportion of oxygen obtained is so much less than that obtained from potassium chlorate that the student should always use potassium chlorate. The cost of oxygen from mercuric oxide varies from 20 to 40 times as much as the cost from potassium chlorate depending upon the relative market costs of the compounds.

38. Reversible Reaction. It is well to notice in connection with the decomposition of mercuric oxide that the reaction is reversible. (See §§ 26 and 188.) The oxide is prepared by heating metallic mercury; it may be either wholly or partly decomposed by heat. If only part of the oxygen is driven off it will take up oxygen again from the air when it is poured from the tube. The equation for the reaction may be written



39. Methods Involving the Use of Light. These are not used practically in the laboratory as a source of oxygen, but may be seen when chlorine water is exposed to light, or when green leaves, such as mint, are placed in a dish containing water charged with carbon dioxide.

40. Methods Involving the Use of Electricity. Oxygen may be obtained by the electrolysis of a dilute acid, such as sulphuric or phosphoric, or by the electrolysis of a salt rich in oxygen such as potassium sulphate or sodium sulphate. When a dilute acid is used the process is *usually called the electrolysis of water*, but as will be found in Chapter 5 *water does not ionize sufficiently to enable it to conduct the electric current*. On the other hand *the dilute acid or salt solution does ionize, conducts the current and is decomposed*, oxygen being set free in both cases, but when a dilute acid is used the oxygen is set free from the *action of a part of the acid upon the water*. Since the oxygen and hydrogen are obtained in the proportion to form water it *looks like the electrolysis of water, but the decomposition of the water is brought*

about by chemical methods. The method is not often used in the small laboratory but is used extensively by firms producing oxygen on a large scale. The oxygen is set free at the positive electrode, therefore acting as a negative or non-metallic element, while the hydrogen is set free at the negative electrode, thus acting as a positive or metallic element. (See §209.)

41. Oxygen from the Action of Chemical Reagents. Certain chemical reagents will evolve oxygen without the use of heat if properly mixed. Hydrogen peroxide when added to salts rich in oxygen, such as potassium permanganate or potassium dichromate, will produce an abundant evolution of oxygen. The two substances each lose oxygen and the atoms of oxygen unite to form oxygen molecules. Water may be dropped upon sodium peroxide (sold under the name of Oxone) and oxygen will be given off very freely. The yield averages 2.2 cubic feet per pound. While these methods are very convenient the materials are more expensive than potassium chlorate and should not be used by the student without special directions.

42. Purification and Collection of Oxygen. The manganese dioxide, often carried over with the gaseous oxygen, may be washed out by passing the gas through a large delivery tube into a bottle partly filled with water. The delivery tube should reach almost to the bottom of the wash bottle so that the gas bubbles up through two or three inches of water. This bottle is fitted with stopper and delivery tube so that after the gas leaves the water, it passes through the second tube to the collecting bottles which are usually filled with water and inverted in the trough. The end of the delivery tube is placed beneath the mouth of the bottle and the escaping gas, being lighter than the water, rises through the water, forcing the latter out of the bottle by pressure. If the oxygen is wanted in a dry condition, it is passed through the U tube or straight tube filled with calcium chloride, which absorbs the water. (See Fig. 9.) It is often sold as a compressed gas in strong steel cylinders, the volume of the gas in the

various sized tanks being sufficient to occupy 50, 100, or 1000 cubic feet at ordinary pressure.

43. Physical Properties.

Pure oxygen is a colorless, odorless, tasteless gas. One liter of the gas weighs 1.429 grams. It is 15.879 times as heavy as hydrogen, and about 1.1 times as

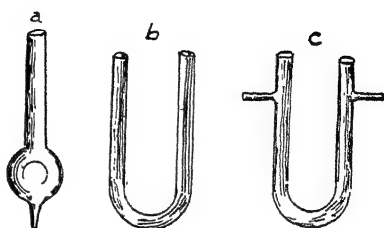


FIG. 9. Calcium Chloride Tubes for Drying Gases.

heavy as air. (Since the molecular weight of the oxygen molecule, O_2 , is 32, and the comparative weight for air is 28.95, the weight of any gas to air may be found readily by dividing the molecular weight of the gas by 28.95.) Oxygen is not very soluble in water, about 4 volumes of the gas dissolving in 100 volumes of water. Since oxygen is not very soluble it is difficult to liquefy, requiring a temperature of -182.5° at ordinary pressure. Liquid oxygen is usually obtained from liquid air by allowing the liquid to stand. The nitrogen boils off at -193° so that after it has stood for a while at a slightly higher temperature nearly pure liquid oxygen remains. (See §81.)

If liquid oxygen is allowed to evaporate rapidly under a pressure of a few millimeters of mercury, part of the liquid is converted into a solid having a temperature of about -227° .

44. Chemical Properties. When substances are burned under ordinary conditions they form oxides. A piece of magnesium ribbon burns brilliantly and forms magnesium oxide, a white powder, which might be called magnesium ash; mercury forms mercuric oxide, a red powder or ash, but frequently the substances formed pass off in a gaseous condition, as when we light a candle, illuminating gas, or alcohol. In all these cases we form oxides, and we say that the substance *burned in oxygen*. We might, however, reverse the conditions and burn oxygen in an atmosphere of illuminating gas, (see Fig. 10) or hydrogen as

easily as we burn illuminating gas, in the ordinary atmosphere or in oxygen. The principle is that the *gases combine* and whenever we have chemical combination with light, we say that one

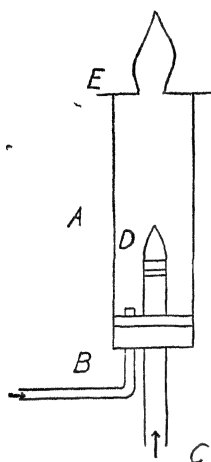


FIG. 10. Oxygen
Burning in Illumi-
nating Gas.

gas burns in the other, but it is better to say that we have a *chemical combination of the two*. In fact, as we shall see a little later, we may have chemical combinations of two substances accompanied by light without having either air or oxygen present in the process. In the ordinary meaning of the words, *oxygen supports combustion but does not burn*.

45. Oxygen Combinations. Oxygen enters into combination with nearly every known substance, the exceptions being fluorine and the rare gases of the atmosphere. In most cases the combination is direct, but as in the case of platinum and nitrogen, the combination must sometimes be brought about by indirect methods. In some the combination is very rapid, as may be seen

when we cut a piece of potassium or sodium, the bright surface becoming dim almost before we are able to see its luster. Perfectly dry phosphorus will not burn in dry oxygen. It is necessary to have traces of water vapor present as a catalytic agent, although it does not seem to take part in the reaction. Powdered willow charcoal burns with brilliant and nearly explosive violence if first heated to redness and dropped into a jar of oxygen. Many powdered metals, such as magnesium, aluminum, zinc or iron will burn with dazzling brilliancy.

46. Oxygen in the Air. Pure air is about 21% oxygen. This may be determined in various ways, one being to burn out the oxygen with a piece of phosphorus held inside a jar inverted over water and after the resulting fumes of phosphorus pentoxide

have reacted with water, the remaining gas is impure nitrogen, and the amount of oxygen present in the air may be determined by measuring the amount of water that has risen in the jar to take the place of the oxygen. The nitrogen in the air is not necessary for life but dilutes the oxygen to prevent too rapid combustion of the tissues. Expired air has nearly 5% less oxygen than fresh air, the oxygen being used to form carbon dioxide, which in itself is not poisonous, but *air containing much carbon dioxide, is usually considered dangerous.* (See §76.)

47. Reduction and Oxidation. When a substance gives up oxygen or any other electro-negative substance so that *the percentage of the metal or more electro-positive element is increased*, the process is called *reduction*. On the other hand *if the percentage of the more electro-positive element or metal is decreased the process is called oxidation*. It should be noted carefully by the student that the names *apply to the process rather than to the electro-negative substance involved*. Thus in a broad meaning it is possible to have a substance oxidized without having any oxygen used in the process. As an illustration of this let us look at the reaction between stannous chloride and mercuric chloride,

stannous chloride mercuric chloride stannic chloride mercurous chloride
 $\text{SnCl}_2 \quad + \quad 2\text{HgCl}_2 \quad \rightarrow \quad \text{SnCl}_4 \quad + \quad 2\text{HgCl} \quad \downarrow$

In this case the stannous chloride has been *oxidized by part of the chlorine* to stannic chloride, *reducing the relative proportion of tin in the compound*, while the mercuric chloride has been *reduced to mercurous chloride*, with an *increase in the proportion of mercury*.

However

ferric oxide carbon monoxide iron carbon dioxide
 $\text{Fe}_2\text{O}_3 \quad + \quad 3\text{CO} \quad \rightarrow \quad 2\text{Fe} \quad + \quad 3\text{CO}_2 \quad \uparrow$

In this case the ferric oxide has been reduced to metallic iron and the carbon monoxide has been oxidized to carbon dioxide.

Or,

copper oxide hydrogen copper water
 $\text{CuO} \quad + \quad \text{H}_2 \quad \rightarrow \quad \text{Cu} \quad + \quad \text{H}_2\text{O}$

Here the copper oxide has been reduced to metallic copper and the hydrogen has been oxidized to water.

In all cases there has been no reduction without a corresponding oxidation.

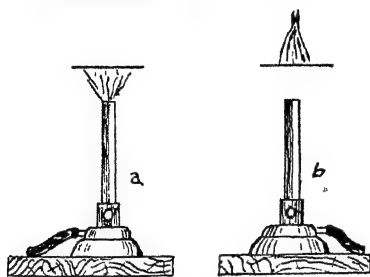


FIG. 11. The Gas Must Reach its Kindling Temperature Before it Can Ignite.

48. Kindling Temperature. Oxidation may be either rapid or slow. *The amount of heat evolved is the same in both cases, but in slow oxidation the heat is not so evident. If the oxidation is rapid the process is called combustion, and this is often accompanied by light, but*

light does not appear until the substance has reached what is called the *kindling temperature* which may be only a few degrees higher than the ordinary temperature, as in the case of phosphorus, but may be several hundred degrees higher. Often the heat generated by the combustion of the substance is sufficient to keep the temperature up to, or above, the kindling temperature, as in burning ordinary illuminating gas and the *combustion is continuous, unless the substance is cooled below the ignition point.* (See Fig. 11.) Some substances, such as oily waste, oxidize slowly, but do not permit the heat to escape readily, so that the heat accumulates, and the temperature gradually rises until the kindling temperature is reached when flames appear and the combustion proceeds more rapidly. This is usually called spontaneous combustion. The same action often occurs in piles

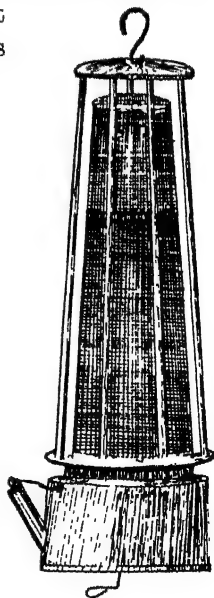
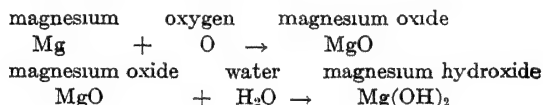


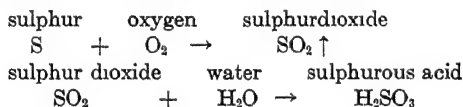
FIG. 12. The Davy Safety Lamp.

of coal. The Davy safety lamp (see Fig. 12) and its many modifications are illustrations of how the surrounding gauze conducts away the heat and prevents the outside gases from reaching the kindling temperature.

49. Classification of Oxides. From the experiments it will be noticed that when we form a metallic oxide by burning a metal in air or in oxygen and dissolve the oxide in water, the resulting solution will turn red litmus solution blue, or give a magenta color to phenolphthalein solution; while non-metals may be burned to oxides, which, when dissolved in water, will turn blue litmus red, or remove the color from reddened phenolphthalein. From this it may be seen that the *oxides of metals usually give hydroxides or bases, thus,*



while oxides of non-metals will give acids, thus,



See also §164.

50. Uses of Oxygen. Oxygen is used in the oxyhydrogen and oxyacetylene burner; it is used in medicine where there is shortness of breath, or in the administration of nitrous oxide, (commonly called "gas" §138). It is absolutely essential for life and for all ordinary combustion, as in a coal, wood or gas fire. It is used in the pulmotor, or lungmotor, to restore consciousness to a person overcome by gas, or when nearly drowned. Compressed oxygen is used in connection with the gas mask for rescue work. Fig. 13 shows a small commercial oxygen generator to use with masks, to revive persons overcome by gas, etc.

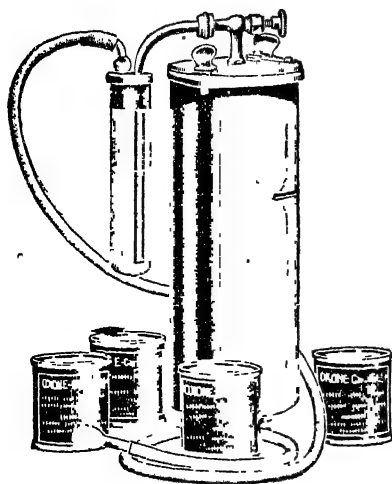


FIG. 13. A Small Commercial Oxygen Generator

51. Commercial Methods of Preparing Oxygen.

The chief commercial processes in use at the present time for preparing oxygen are (1) the liquefaction of the air, which is allowed to stand until the nitrogen boils off; (see §81); and (2) the electrolysis of dilute sulphuric acid; (see §209.)

OZONE

52. Ozone is Very Closely Associated with Oxygen.

The name of the gas comes from the Greek, meaning "to smell." There

are numerous methods of preparing ozone but the simplest is to place a test tube over one of the electrodes of a Toepler-Holtz or Wimshurst electrical machine, separate the electrodes about an inch, and pass the spark through the glass. A small portion of the oxygen of the air contained in the test tube is turned to ozone. It is formed during thunder storms, and is said to exist in the air in very minute quantities at all times.

53. Properties. Ozone has a strong, peculiar odor, somewhat resembling sulphur dioxide, but not as suffocating, although when inhaled in small quantities it affects the membranes. It may be condensed by cold and pressure to a sky-blue liquid that boils at -119° , about the critical temperature of oxygen. When ozone is heated to 290° it is transformed into oxygen, and the volume of the latter gas is 50% more than the volume of the ozone used, showing that the molecular formula for ozone is O_3 . Ozone is more soluble than oxygen. Even at moderate temperatures ozone is a vigorous oxidizing agent,

acting upon many bodies that react only feebly with oxygen, if at all, such as indigo, silver, etc. It decomposes potassium iodide, setting the iodine free, so that filter paper saturated with starch paste and potassium iodide serves as ozone test paper, by turning blue in the presence of ozone. A very delicate test for ozone is fluorescein solution, having a strength of 1 part in 1,000,000. The fluorescent color is destroyed by the action of the ozone, and it has been estimated that as little as 1/1,000,000 milligram of ozone can be detected by this method.

54. Relation of Ozone to Oxygen. The oxygen molecule is O_2 , while that of ozone is O_3 , showing that the molecular weight must be 48 instead of 32. It is 50% heavier than oxygen, and it is thought that the three atoms of oxygen forming the ozone molecule are compressed into the same space as that occupied by the two atoms in the oxygen molecule. Its vigorous oxidizing properties make it good for bleaching, deodorizing or purifying. It is frequently used to purify the air of crowded buildings, such as theaters.

55. Allotropy. The occurrence of an element in two or more forms is called allotropy, so that ozone is an allotropic modification of oxygen. Various other substances have the same peculiar property, carbon, phosphorus and sulphur being the best known examples.

56. Problems. *Molecular Weight and Percentage Composition.*

(1) To find the molecular weight of a compound from the formula it is necessary to know the exact composition of the compound; the atomic weight of each element in the compound, and the number of times each element is taken. The atomic weight of each element in the compound is multiplied by the number of times the element is taken and the sum of these products gives the molecular weight. Thus to find the molecular weight of nitric acid, HNO_3 , we add the atomic weight of hydrogen to the atomic weight of nitrogen and then add 3 times the atomic weight of oxygen, obtaining $1+14+48=63$. In the same manner the molecular weight of sodium hydroxide, $NaOH$, is $23+16+1=40$; while that of sulphuric acid, H_2SO_4 , is $(2 \times 1) + 32 + (4 \times 16) = 2 + 32 + 64 = 98$.

(2) To find the percentage composition of a compound first find the molecular weight as explained above. Then multiply the atomic, or mul-

tiple atomic, weight of each element by 100 and divide the product by the molecular weight of the compound. If no more zeros are added the result gives the percentage in whole numbers. When the multiplication by 100 is omitted the result is in hundredths, meaning that percentage. Thus the percentage composition of sodium hydroxide is found as follows:

$$\frac{23 \text{ (at. wt. of Na)} \times 100}{40 \text{ (mol. wt. of NaOH)}} = 57.5\% \text{ of sodium}$$

$$\frac{16 \text{ (at. wt. of O)} \times 100}{40} = 40\% \text{ of oxygen}$$

$$\frac{1 \text{ (at. wt. of H)} \times 100}{40} = 2.5\% \text{ of hydrogen}$$

$$57.5\% + 40\% + 2.5\% = 100\%$$

The percentage of each element in sulphuric acid is found thus:

The molecular weight of $\text{H}_2\text{SO}_4 = 98$.

$$\text{The percentage of hydrogen} \quad \frac{2 \times 100}{98} = 2.04081$$

$$\text{The percentage of sulphur} \quad \frac{32 \times 100}{98} = 32.65306$$

$$\text{The percentage of oxygen} \quad \frac{64 \times 100}{98} = 65.30612$$

$$\text{Total for } \text{H}_2\text{SO}_4 = 99.99999$$

The total very seldom equals exactly 100 owing to unfinished divisions.

1. Referring to the formulas of the substances given in the equations of this chapter, find the molecular weight of each compound. (Additional compounds may be selected from other parts of the text.)

2. Find the percentage composition of the substances used in the preceding problem.

3. Which contains more hydrogen and how much—25 grams of hydrochloric acid or 25 grams of sulphuric acid?

4. Arrange the following oxides of iron in the order of richness in iron: FeO ; Fe_2O_3 ; Fe_3O_4 .

5. If potassium chlorate, KClO_3 , sells for 15 cents per pound, and mercuric oxide, HgO , for \$1.20 per pound; taking the percentage of oxygen and the cost both into account which of these compounds should be used in the laboratory for obtaining oxygen? What was the relative cost? If the price of KClO_3 advanced to \$1.00 per pound and that of HgO to \$4.00 what would be the ratio of expense using these same substances for oxygen?

CHAPTER III

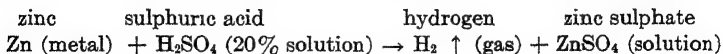
HYDROGEN

SYMBOL, H; VALENCE, 1; ATOMIC WEIGHT, 1.008

57. Occurrence. Like oxygen, hydrogen occurs both *free and combined*; but differs from oxygen by being found *almost exclusively in a combined form*. Free hydrogen occurs in very small quantities in the gases that issue from oil and gas wells and from active volcanoes; in the atmosphere of the sun and fixed stars; and in meteorites. It is thought that hydrogen exists in large quantities in the extreme upper atmosphere. *Combined hydrogen, however, is very abundant*. It is found combined in all *acids and alkalies*; it forms $2/3$ of *water* by volume, and is found in thousands of *carbon compounds*, such as illuminating gas, oil, alcohol, sugar, starch, cellulose, etc.

58. Preparation of Hydrogen. Since hydrogen is found almost entirely in compounds, we must decompose these substances in order to obtain it. The substances yielding hydrogen abundantly and cheaply are the *common acids, alkalies and water*. The methods differ in detail according to the substance we use.

59. Hydrogen from Acids. Only two acids are used for obtaining hydrogen—dilute sulphuric and hydrochloric. Nitric acid is not used because generally the hydrogen liberated attacks the acid and gives other substances instead of hydrogen. (See §135.) The common method is to cover mossy (granulated) zinc with dilute sulphuric acid, 1 part of the acid being used with 4 parts of water. (See Fig. 14.) *The zinc does not dissolve in the acid, but reacts chemically with it, displacing the hydrogen and combining with the acid radical, SO₄, to form zinc sulphate*



The hydrogen does not react with either the remaining sulphuric acid, that has not taken part in the reaction, nor with the zinc sulphate, and is, therefore, evolved as a gas. The zinc sulphate remains in solution in the water that was used to dilute the sulphuric acid, and may be obtained as crystals of zinc sulphate by slowly evaporating the water. If the zinc had

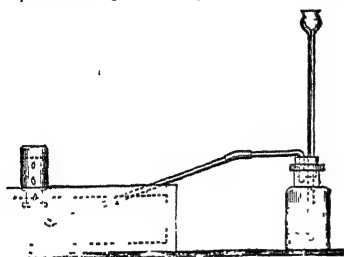
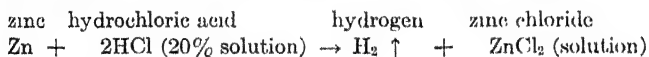


FIG. 14. Preparation of Hydrogen from the Action of Zinc with Sulphuric Acid.

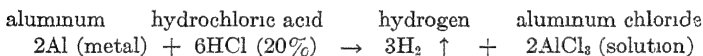
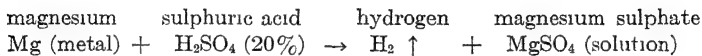
dissolved in the acid we would obtain crystals of zinc, instead of zinc sulphate, and we would not have obtained hydrogen any more than when we dissolve salt or sugar in water. The action between the zinc and the acid is chemical in its nature.

We might have used dilute hydrochloric acid instead of the sulphuric acid and our equation would then read:



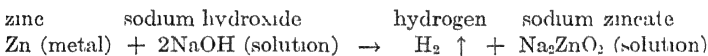
The fundamental principle is exactly the same—the *displacement of the hydrogen by the metal*, which is chemically *more active than the hydrogen*. Any one of several other metals might have been used instead of the zinc. If we examine the table of chemical activity given in §36 we find that hydrogen stands *below lead and above copper*. Lead and all of the metals above it in the table are, therefore, more active chemically than hydrogen, and hence can displace it from dilute sulphuric and hydrochloric acids, while copper and all the metals below it are less active chemically and cannot displace hydrogen from dilute acids. As the metal approaches the more active end of the table the reaction with hydrogen becomes more violent. Zinc is sufficiently active to give a rapid stream of hydrogen, and at the same time

is so much cheaper than any of the more active metals, that it is almost invariably used in the laboratory. If one of the other metals is used instead of the zinc the general style of the equation is the same with the change in the metal and the corresponding salt formed.

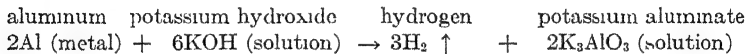


Metals more active than hydrogen are not found free in nature. Less active metals may be found free. Since metals react with acids they are known as base-forming elements. Hydrogen may also be obtained from dilute acids by electrolysis, as described in §209.

60. Hydrogen from Alkalies. Some of the metals will also react with some of the alkalies with the evolution of hydrogen and the formation of a salt. We may notice the reaction of zinc with sodium hydroxide



Potassium hydroxide might be used instead of sodium hydroxide with the formation of the corresponding potassium zincate; or we might use aluminum instead of the zinc with either of the hydroxides, forming the corresponding aluminates—

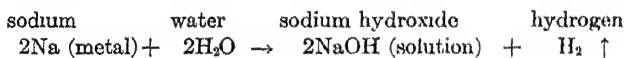
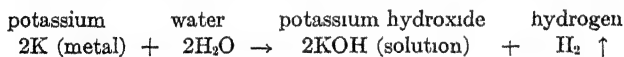


The corresponding salt formed when sodium hydroxide is used is sodium aluminate, Na_3AlO_3 .

When zinc and aluminum react with bases, such as sodium hydroxide or potassium hydroxide, they act as acid forming elements.

These methods are not commonly used, but are used in certain tests when very pure hydrogen, free from hydrogen sulphide and arsenic is wanted.

61. Hydrogen from Water. Several of the more *active metals will react with water*, setting part of the hydrogen free, and combining with the rest of the hydrogen and the oxygen to form a metallic hydroxide. The most active metals react the most violently, the reaction with *potassium producing sufficient heat to ignite the hydrogen even in cold water* as fast as it is formed. The reaction with sodium is not so violent, and the hydrogen is usually not ignited, except when warm water is used.



Calcium is less energetic than sodium, the reaction occurring in cold water, but better in warm. The calcium, moreover, does not float like potassium and sodium, but sinks to the bottom and reacts rapidly without melting.

Hydrona cubes consist of an alloy of sodium and lead and yield 2.6 cubic feet of hydrogen per pound when placed in water.

If we use such metals as *iron, zinc or magnesium* it is necessary

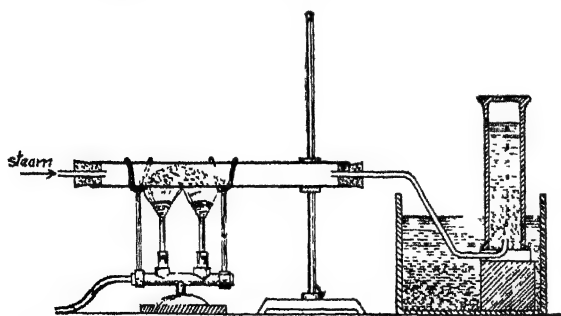


FIG. 15. Preparation of Hydrogen from the Action of Iron with Steam.

to have the water in the form of steam and the metals should be placed in a tube and heated to redness. (See Fig. 15.) The steam is then passed

through the tube and the reaction is similar to that of the more active metals.

Superheated steam may be passed over red hot coke and we will obtain hydrogen mixed with carbon monoxide. The carbon monoxide may be separated from the hydrogen by passing the mixed gases first over nickel to form nickel carbide and carbon dioxide, and then through lime water where the carbon dioxide will form a precipitate of calcium carbonate by uniting with the calcium hydroxide. This method is not suitable for the small laboratory, but, when considerably modified, is used extensively in commercial chemistry to form water gas, the mixture being enriched by spraying it with heavy hydrocarbons, after which it is sold as illuminating gas. No nickel or lime water is used in the commercial process. (See § 817.)

62. Purification and Collection of Hydrogen. Laboratory hydrogen has an odor, owing to the impurities it contains. It may be purified by passing it through sodium hydroxide and potassium permanganate solutions. If the gas is wanted dry it should be passed through a tube containing anhydrous calcium chloride (calcium chloride containing no water) as with oxygen. When dryness is not essential it is usually collected over water the same as oxygen, but may be collected in a dry receiver held mouth downward, while the delivery tube is passed to the highest part of the receiver. If the gas is to be burned it is *absolutely essential to know every time that the gas is not mixed with air*. If the hydrogen is mixed with air or with oxygen before it is ignited, *violent explosions occur*.

63. Physical Properties. Pure hydrogen is colorless, odorless and tasteless. It is the lightest gas known, one liter under normal conditions weighing 0.089873 gram. Air is about 14.475 times as heavy as hydrogen; water 11,000 times; and platinum, the heaviest of the common metals, is about 236,500 times as heavy. Since hydrogen is the lightest of all known substances, its vapor density is taken as 1.

Hydrogen is not very soluble in water, only 0.193 volumes dissolving in 100 volumes of water at ordinary temperatures. The gas may be reduced to a liquid at -252.5° and 13 atmospheres pressure. Liquid hydrogen when evaporated rapidly, solidifies in part, the solid having a temperature of about -260° .

Hydrogen diffuses through porous substances faster than any other gas. At high temperatures it passes through plates of iron and platinum, and passes rapidly through thin sheets of rubber, making it very difficult to keep it any length of time.

64. Chemical Properties. Since hydrogen acts chemically as a metal in direct combinations we would naturally expect it to combine with non-metals. When mixed with fluorine it combines with explosive violence, even in the dark. With chlorine it will explode in the sunlight. It also combines directly with oxygen, burning with a nearly colorless flame to form water. (See also §112.) Hydrogen combines directly or indirectly with a large number of elements, such as carbon, to form hydrocarbons; with nitrogen, to form ammonia; with sulphur, to form hydrogen sulphide, etc. These combinations will be explained more fully where the compounds are studied

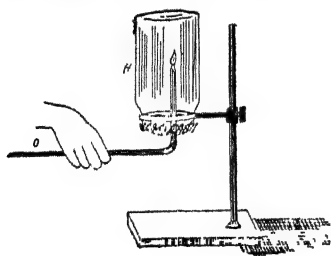


FIG. 16. Oxygen Burning in an Atmosphere of Hydrogen.

Hydrogen is not a supporter of combustion in the ordinary sense of the term—that is, such substances as wood, paper, etc., cannot burn in it; but we may burn a stream of chlorine in hydrogen. This is merely the chemical combination of the two without the presence of oxygen being necessary. Just as we can burn a

stream of hydrogen in air or in oxygen, so we can burn a stream of air or oxygen in hydrogen. (See Fig. 16.)

Hydrogen may be mixed with oxygen and kept for years at ordinary temperatures without chemical combination, but as

the temperature increases the gases begin to combine, and the combination occurs with explosive violence at 700° unless the gases are both perfectly dry, when combination does not occur even at that temperature. Only very small portions of hydrogen and oxygen should be mixed together before igniting the mixture, since the explosion occurs with great violence, and the speed of the explosion is at the rate of about 2810 meters, or about 1.75 miles per second. The greatest violence is obtained when two volumes of hydrogen are mixed with one of oxygen.

65. Commercial Applications. The combination with oxygen may be conducted quietly if the two gases are not mixed until after the hydrogen is lighted. This is best brought

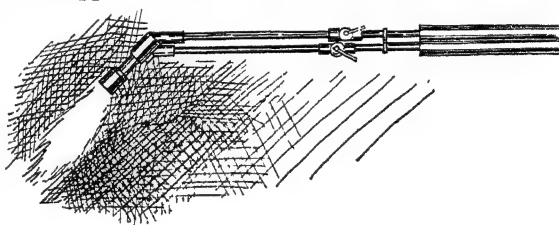


FIG 17. Oxyhydrogen Blowpipe.

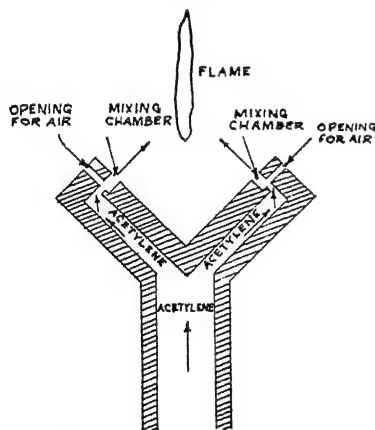


FIG 18. Acetylene Flame.

about by the use of oxyhydrogen blowpipe, (see Fig. 17) where the hydrogen is in the outer tube, and the oxygen is conducted through the inner tube to the burning hydrogen. The temperature is estimated at from 3000° to 3500° . The acetylene flame is very bright but requires a special burner so that the air supply is sufficient for complete combustion. (See Fig. 18.) The *oxyacetylene* flame is, however, still hotter than the oxyhydrogen flame by nearly 500 degrees. The

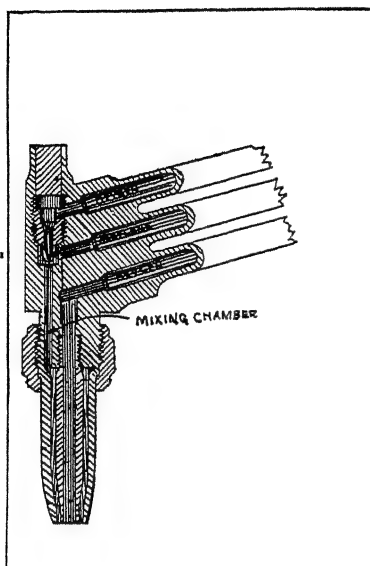


FIG. 19. Oxyacetylene Burner for Cutting Steel.

reason for this is that the decomposition of the acetylene is accompanied by the evolution of a large amount of heat and this is added to the heat produced by the combustion of both the hydrogen and the carbon of the acetylene, making it possible to cut through thick plates of steel in less than one minute. (See Fig. 19.) Still later methods employ the oxyblau-gas and oxyoil-gas, made from cracking heavy oils, instead of acetylene. The flame is almost as effective and is more easily controlled.

Compare these powerful

flames with the flame of a paraffin candle. (See Fig. 20.)

66. Nascent Hydrogen, or hydrogen that is just being set free from its combinations, is frequently used in the laboratory to bring about reductions where the ordinary stream of molecular hydrogen will not affect the substance used. The atomic or ionic hydrogen thus obtained is more active than the molecular hydrogen where part of the activity is utilized in holding the atoms together to form the molecule. Nascent hydrogen and nascent chlorine are used in the same manner, the gas being set free in the mixture upon which they are to act.

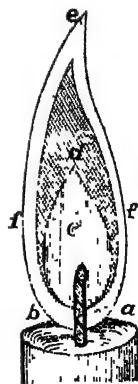
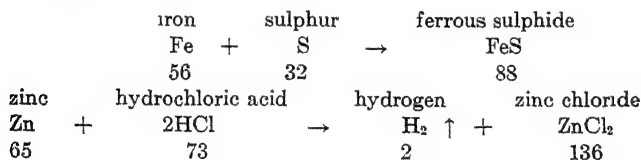


FIG. 20. A Candle Flame.

67. Other Uses of Hydrogen. Since hydrogen is the lightest of all gases, it is used for filling balloons and the gas bags of air ships, giving them the greatest available uplift, but it is very dangerous on account of being so explosive and helium (§75) should be used instead, since it has about 93% of the available uplift of hydrogen and is absolutely non-explosive. Hydrogen was formerly used extensively in stereopticon work as the lime, Drummond or calcium light—an oxyhydrogen flame striking against a cylinder of quick lime (calcium oxide), but it is not used as much now since the electric arc is so much more efficient, the candle power of the lime light being only about 800 while that of the electric arc may be 2000 or more as determined by the amperage. Hydrogen is also used extensively to make non-edible oils and fats fit for human consumption. (See Chapter 25.)

68. Problems. When two or more substances react, to find the reacting weights, and the weights of the products.

The equation is first written correctly so that the valence is fully satisfied. The atomic, multiple atomic, molecular or multiple molecular weights of the substances are then taken as the reacting weights and the weights of the products. Thus



These should be read thus, "Fifty-six grams of iron will react with 32 grams of sulphur to produce 88 grams of ferrous sulphide," or "Sixty-five grams of zinc will react with 73 grams of hydrochloric acid to produce 2 grams of hydrogen and 136 grams of zinc chloride." Any other unit of mass as kilogram, ounce, pound or ton could be used in place of the gram, since the proportion would be the same.

Find the reacting weights and the weights of the products in the following equations:

1. $\text{KOH} + \text{HNO}_3 \rightarrow \text{H}_2\text{O} + \text{KNO}_3$
2. $\text{KOH} + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{KCl}$

3. $2\text{KOH} + \text{H}_2\text{SO}_4 \rightarrow 2\text{H}_2\text{O} + \text{K}_2\text{SO}_4$
4. $\text{NaOH} + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{NaCl}$
5. $\text{NH}_4\text{OH} + \text{HC}_2\text{H}_3\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{NH}_4\text{C}_2\text{H}_3\text{O}_2$
6. $2\text{NH}_4\text{OH} + \text{H}_2\text{SO}_4 \rightarrow 2\text{H}_2\text{O} + (\text{NH}_4)_2\text{SO}_4$
7. $\text{Ca}(\text{OH})_2 + 2\text{HNO}_3 \rightarrow 2\text{H}_2\text{O} + \text{Ca}(\text{NO}_3)_2$
8. $\text{Ca}(\text{OH})_2 + \text{H}_2\text{SO}_4 \rightarrow 2\text{H}_2\text{O} + \text{CaSO}_4$
9. $\text{Ca}(\text{OH})_2 + 2\text{HC}_2\text{H}_3\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$
10. $2\text{NaOH} + \text{H}_2\text{SO}_4 \rightarrow 2\text{H}_2\text{O} + \text{Na}_2\text{SO}_4$

CHAPTER IV

NITROGEN AND THE ATMOSPHERE

NITROGEN. SYMBOL, N. ATOMIC WEIGHT, 14.01.

VALENCE, 3 and 5

69. Occurrence. Nitrogen occurs free in the air, of which it is about 78% by volume and about 75.5% by weight. Combined nitrogen occurs in all nitrates, nitrites, ammonium compounds, in many carbon compounds, and in nearly all animal substances. Atmospheric nitrogen as obtained in the laboratory is mixed with small amounts of argon, neon, xenon, krypton and helium, the last five gases having been discovered between 1894 and 1898.

70. Preparation. Nitrogen may be prepared either by separating it from the other gases of the atmosphere or by decomposing some of its compounds. As prepared in the laboratory it is always very impure, unless purified after it is obtained. The customary method is to burn the oxygen from a limited amount of air by means of a small piece of phosphorus. (See Fig. 21.)

It may also be obtained from the air by absorbing the oxygen in an alkaline solution of potassium pyrogallate.

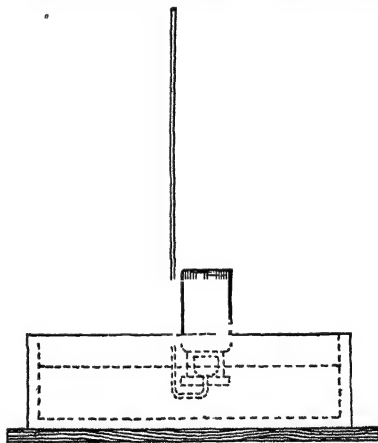
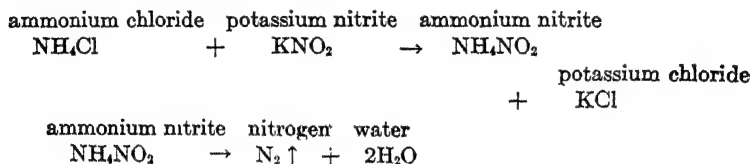


FIG. 21. Preparation of Nitrogen.

It may be prepared in a much purer form by decomposing certain of its compounds. Ammonium nitrite is often used for this purpose, and it may be made and decomposed in one operation by heating in a test tube a mixture of ammonium chloride and potassium nitrite, moistened with a little water. The gas is passed through a delivery tube and collected over water. The reaction may best be represented by two equations, the first showing the formation, and the second the decomposition of the ammonium nitrite:



71. Physical Properties. Nitrogen is a colorless, odorless, tasteless gas, having a specific gravity of 0.9673 (air = 1). One liter of the gas weighs 1.2514 grams if pure. Atmospheric nitrogen is heavier because of the presence of the other gases. About 2 volumes of nitrogen will dissolve in 100 volumes of water, the exact amount depending upon the purity of the gas and the temperature. Nitrogen may be reduced to a liquid at -194° under normal pressure. On further cooling it becomes a white solid that melts at -211° .

72. Chemical Properties. Nitrogen is very inert. It neither burns nor supports combustion. It does not combine directly with oxygen, and does not combine readily with any substances except at high temperatures, and then with only a few, such as magnesium, lithium, calcium, boron and silicon. The combination with magnesium, for example, gives magnesium nitride, Mg_3N_2 . Nitrogen may be made to combine with oxygen when powerful electric sparks are passed through the mixture. This is known as the fixation of atmospheric nitrogen, and will be described in Chapter 29. Nitrogen also combines directly with hydrogen to form ammonia, under proper conditions of tempera-

ture and pressure, when selected catalytic agents are used. (See §127.) From these illustrations it may be readily seen that free nitrogen is not an active element, and that the old French name "Azote," meaning "without life," was logically applied. On the other hand, when we study the compounds of nitrogen, we shall find that it acts in an entirely different manner. Nitrogen in a combined state is found in nearly all of the powerful explosives, the most brilliant dyes, the most violent poisons, the habit-forming narcotics, such as opium, and in many other active compounds. The gas "without life" has become the exact opposite.

73. Uses of Nitrogen. Free nitrogen is in the air apparently for the chief purpose of diluting the oxygen. Combined nitrogen plays a powerful part in many compounds. The description of these compounds and the methods of preparing them will be found in several of the later chapters.

THE AIR OR ATMOSPHERE

74. Composition of Air. Air is composed of several gases mixed together. The chief ones are oxygen, nitrogen, argon, carbon dioxide and water vapor. The first three are found in almost unvarying proportions, but the last two and the rare gases of the air vary in amount according to conditions. Oxygen constitutes about 20.93% of the air by volume, or 23.13% by weight. Nitrogen and its companion gases make up the rest of the air, and of this amount argon is about 0.94% by volume and about 1.3% by weight. Carbon dioxide forms about 0.03% except in expired air, where it may reach 4% or more. Water vapor will vary with the temperature, pressure and the direction of the wind. Other gases found mixed with the nitrogen are helium, neon, xenon and krypton. In addition to these small amounts of ozone, hydrogen, hydrogen dioxide, ammonium nitrate, dust, bacteria, etc., are found in various localities. Tests on air covering a year show that from 56 to 950 tons of dirt are deposited upon each square mile from the air annually.

In England careful estimates have been made on the subject of polluting the air by smoke. At Leeds it has been estimated that free mineral acids in smoke may amount to 80 pounds per acre. This affects vegetation, lowering the lime content of the soil and is very injurious. The value of the products in some cases has been reduced to one-sixth of their former value. In London it is estimated that between 6 and 9 o'clock in the morning enough smoke comes from the various chimneys to give 200 tons of free carbon and that a smoke cloud 400 feet high, covering London, contains at least 200 tons of carbon. The same general conditions occur in many of our large cities where bituminous coal is burned without the proper use of smoke consuming devices.

At higher altitudes, the air is not the same as at the surface. It has been estimated that at a height of 30 miles the percentage of oxygen has diminished to 10; while at 90 miles, the air is thought to contain only 1% of oxygen; 11.1% of hydrogen and about 88% nitrogen; and at 120 miles, no oxygen, 0.6% nitrogen, and 99.4% hydrogen, becoming all hydrogen at 180 miles; but at such altitudes there is very little of any gas. If hydrogen is absent in the atmosphere above 150 kilometers—about 90 miles—it is thought that the atmosphere at that height is almost entirely helium.

75. Of the Newly Discovered Gases, argon, neon and helium are the most important. *Argon* is used in the Tungsar lamps, the important part of the tungar rectifier for changing the alternating current to the direct. The glass bulb, about the size of an ordinary electric light bulb, is filled with argon at a suitable pressure. The alternating current enters the lamp through a disk anode of graphite, and flows in one direction to a low voltage cathode of tungsten, yielding from about 7.5 to 75 volts D. C. from 110 volts A. C. according to the size of the rectifier.

Neon is of interest because of its use in illuminating. The first neon tubes were made 6 meters long, and yielded a pink light when the electric current was passed through them. Later

neon lamps contain 75% neon and 25% helium. The cathode is an alloy of 82% thallium and 18% cadmium. The anode is of iron. It is rated as a 1/2 watt lamp with a life of 2,000 hours. It produces penetrating red rays and since no blue waves are present in the light from a neon tube, blue objects appear black. When light from a neon tube is combined with light from a mercury vapor tube, which is rich in blue and deficient in red, objects may be seen in their true colors. Neon lights are used in London and Paris for making illuminated street signs.

A new neon lamp known as the Pintsch neon glow lamp requires only a fraction of a milliampere to produce a light effect. The resistance of the glow lamp decreases as the current increases, contrary to Ohm's law. The cathode of the direct current lamp is an iron spiral and the anode is an iron disc.

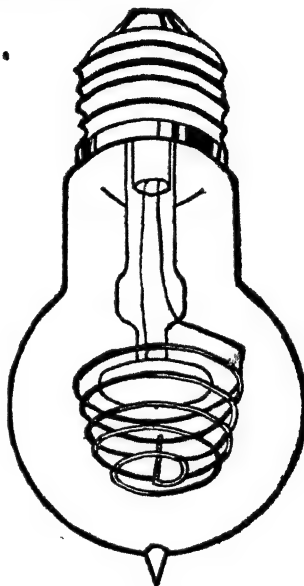


FIG. 22. Neon Lamp.

When a little mercury vapor is present it will also operate on an alternating current. With the direct current only the cathode glows while with an alternating current both electrodes glow. (See Fig. 22.) Neon lamps have been found valuable for signaling purposes and there are numerous other applications. In series with a 100,000 ohm selenium cell on a 220 volt circuit the neon lamp will remain dark as long as the cell is not exposed to light. When the cell is illuminated its resistance drops and the current through the neon glow lamp increases and the glow increases in intensity. If connected in series with an X-ray tube

the neon lamp will indicate by its brightness the amount of current passing through the tube.

Neon is now being used in tubes as ignition gages. The neon in the tube glows when brought into contact with spark plugs and other compounds where a current is passing, making it easy to trace defects in ignition in gasoline engines and the tubes may be used also to detect static charges on belts, doors, machinery, etc., not properly grounded and are especially valuable where inflammable gases are present. A neon tube glows when applied to the outside of the insulation on wires carrying 2,000 volts or more, serving to detect the presence of dangerous currents and the use of neon tubes will probably be further extended.

Since neon is found to the amount of 1 part in 66,000 of air, a liquid air plant producing 50 cubic meters of oxygen per hour can produce approximately 100 liters of neon per day.

Helium, (meaning the sun) is found in small amounts in the air and in the atmosphere of the sun and the fixed stars, in several rare minerals, in some springs, in natural gas, and in meteorites. It is very inert and is more insoluble in water than any other gas, and also the most difficult to liquefy, requiring a temperature of -271.3° , the lowest temperature thus far obtained. Helium is now being used as a substitute for hydrogen in filling the gas bags of balloons and air ships. It has only one atom to the molecule while hydrogen has two, so that the atomic weight of helium is the same as the molecular weight—4; while the atomic weight of hydrogen is 1 and the molecular weight is 2. Since the air is 14.475 times as heavy as hydrogen, the available uplift of helium may thus be seen to be approximately 93% of that of hydrogen. Since helium is absolutely non-explosive, not combining with either the air or any other known substance, it is the most suitable gas for balloons and air ships. Though found in very small amounts normally in the air the gas wells of southern Kansas and northern Texas yield nearly 2% of helium.

The helium is separated by liquefaction of the rest of the gas, which is then vaporized with a marked improvement in its burning qualities. Up to April, 1918, not over 100 cubic feet of helium had been produced at a cost of \$1700 to \$2000 per cubic foot. In a little over a year the government produced 200,000 cubic feet of 92.5% helium, at a cost of about \$5 per cubic foot. The present cost is about 10 cents per cubic foot. The gas is stored in steel cylinders under a pressure of 1 ton per square inch. Each cylinder holds 200 cubic feet of normal pressure helium. Since helium is of such importance in war work, it is to be hoped that the process of storing helium will continue indefinitely. The gas wells of Europe yield only a very small percentage of helium, thus giving the United States almost a monopoly. Helium is also produced in minute quantities when radium disintegrates. (See §530.)

76. The Two Most Important Variable Elements in the atmosphere are carbon dioxide and water vapor. Carbon dioxide usually exists in the proportion of 3 or 4 parts in 10,000, but this is greatly increased in poorly ventilated rooms. Its presence may be shown by lime water or by baryta water, which will become covered with a white film of calcium or barium carbonate. The carbon dioxide itself does not do any serious damage, since it is not poisonous, but its presence usually shows that the air has been breathed. Some recent investigators of the subject of ventilation claim that we do not need a large amount of fresh air if the air in the room is kept reasonably cool and in constant circulation, so as to keep the skin dry by the removal of perspiration, and say that the effects of poor ventilation are due to physiological disturbances caused by interference with elimination of the heat of the body, corresponding closely to fatigue phenomena.

It is now generally believed that workmen breathing air containing small amounts of sulphur dioxide, chlorine, bromine, hydrogen sulphide, chloropicrin, phosgene, etc., are more

immune to diseases affecting the respiratory passages, than those who are not exposed to such air.

77. The Amount of Water Vapor, varies with the temperature, the atmospheric pressure, and the direction of the wind. At ordinary temperatures 100 liters of air will hold about 2 grams of water in the form of vapor, of which 1.7 grams will be deposited as rain if the temperature is cooled to the freezing point of water. The absolute amount is not as important as the relative amount required to produce saturation. The presence of water in the air may be shown by exposing a piece of potassium hydroxide to the air. It often absorbs enough water in an hour or so to dissolve. As the amount of water vapor in the air increases, the barometric pressure decreases, showing that moist air is lighter than dry air, since the molecular weight of water is only 18, while the molecular weight of nitrogen is 28 and of oxygen is 32, giving an average for air of 28.95.

The dust in the atmosphere may be seen when a beam of sunlight enters a partly darkened room. In dustless air the beam is nearly invisible. If there were no dust in the atmosphere there would be no clouds nor rain.

Much of the dust in the atmosphere comes from the smoke and fine dust issuing from factory chimneys. This can usually be overcome to a large extent by the use of the Cottrell precipitator which sends a powerful static charge through the smoke causing it to fall to the bottom of the chimney.

The efficiency of Cottrell precipitating process varies from about 86% in carbide furnaces to 99.99% on brown coal combustion gases. The apparatus works without difficulty at 850°. About fifty plants are working in Germany, about 100 in United States and about 50 elsewhere in the world.

Such substances as fruit juices, when exposed to the air, soon begin to ferment, thus proving the presence of micro-organisms. The air contains only 4 or 5 bacteria per liter, while natural soil contains about 100,000 per cubic centimeter, and good, unfiltered river water contains 6,000 to 20,000 per cubic centimeter.

78. The Percentage of Oxygen in the Air, is determined in various ways. An easy method is to burn a small piece of yellow phosphorus in a limited supply of air, as in a bottle with the mouth dipping under water. The water will rise in the bottle to take the place of the oxygen removed, and by dividing the quantity of water in the bottle by the capacity of the bottle the percentage of oxygen may be approximated. A more accurate method uses an alkaline solution of potassium pyrogallate. This is poured into a tube of air and the end stoppered. The tube is rotated a few times until the oxygen is all absorbed, and the stoppered end is then placed under water and the stopper removed. Water rises to take the place of the absorbed oxygen and the percentage is determined in the same manner as when phosphorus is used.

79. Physical Properties of Air. Air is colorless, odorless and tasteless when pure. Like all gases it is elastic, thus allowing expansion and contraction. Under standard or normal conditions one liter of air weighs 1.293 grams. It is 14.475 times as heavy as hydrogen, and $1/773$ as heavy as water. The pressure of the air at the sea level will balance a column of mercury 760 millimeters high at 0°C in the latitude of New York City, and these are taken as standard conditions of measurements. (See Fig. 23.)

If the temperature is any other than 0°C , and the pressure is any other than 760 mm., they must be reduced to standard conditions in order to secure uniformity of results. In the English system the height of the standard barometer is 30 inches,

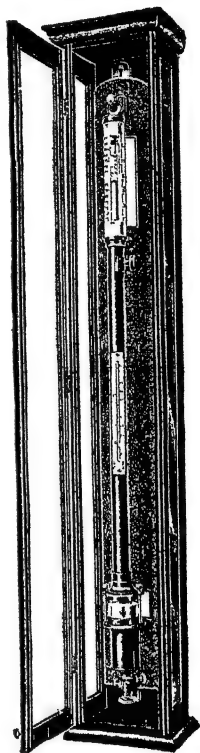


FIG. 23. Standard Barometer.

the pressure is expressed as 14.74 (approximately 15) pounds per square inch, and the temperature is 32° F.

80. To Prove That Air is a Mixture and Not a Chemical Compound.

(1) Nitrogen and oxygen may be mixed and left indefinitely without any evidence of chemical union. The mixture can not be told from air.

(2) Liquid air does not have the same composition as gaseous air. When first made it is about 50% oxygen. The nitrogen boils out first at a temperature of -193° , until finally the liquid air may be 90% oxygen.

(3) When air is dissolved in water the oxygen dissolves about twice as rapidly as the nitrogen. Air expelled from water is about 35% oxygen by weight instead of about 23%.

(4) The composition of the air varies slightly from time to time and in different localities. The composition of a compound does not vary.

(5) Chemically the air acts just the same as free oxygen, but more slowly. This may be shown by the oxidation of phos-

phorus, potassium, etc.

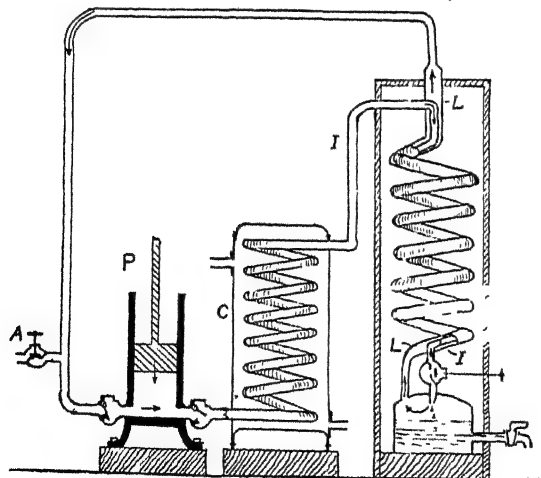


FIG. 24. Linde Liquid Air Apparatus.

81. Liquid Air. Air is liquefied by pressure and cooling. (See Fig. 24.) It is first passed through sodium hydroxide solution to remove the carbon dioxide, then over calcium chloride

to dry it. It is then passed into coils of copper pipe and subjected to a pressure of 120 to 140 atmospheres. The copper pipe is confined in a vessel whose walls are protected against the passage of heat by non-conducting materials. The pressure upon the gas raises the temperature of the air in the coils, which are next cooled to -80° by means of solid carbon dioxide. The air is then allowed to pass through a very small opening and the sudden removal of pressure causes a further reduction of the temperature. As the air escapes it is passed back over the pipes that contain the compressed air, and by repeating the process several times without interruption the air finally issues from the opening in a liquid condition. The receiving vessel has double or triple walls, the air between them being exhausted to about 0.5 mm. (See Figs. 25 and 26)

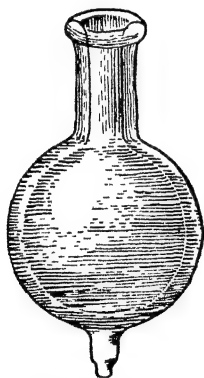


FIG. 25. Double
Walled Dewar
Bulb for Liquid
Air.

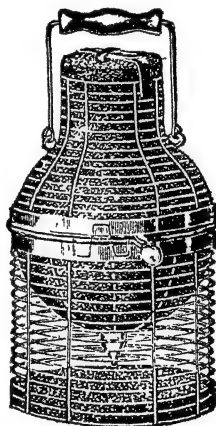


FIG. 26. Carrying
Case for Dewar Bulb.

This prevents heating the air from the outside and it is possible to keep the air for some time provided an opening is left at the top for the escape of the gases as the air vaporizes.

82. Properties of Liquid Air. Liquid air is colorless, with a specific gravity about the same as that of water. It boils at -190° and when placed on ice acts the same as water on a red hot stove. Elastic substances placed in liquid air become as brittle as thin glass. Lead becomes stiff, sonorous and rigid, while alcohol freezes to a white taffy-like mass. When liquid air is poured upon glowing charcoal, the latter burns with explosive violence. An ordinary tin basin placed in the liquid may be crushed like an egg shell. The hand may be dipped into the liquid without injury if removed instantly, since the thin film of air that surrounds the skin prevents the freezing of the flesh. Liquid air explodes violently when confined, easily bursting a steel cylinder.

Numerous practical uses of liquid air have been suggested, but they are still more theoretical than practical. For use in explosive shell it is difficult to control and the inconveniences of trying to manufacture it on a battle field, or of transporting it to the field of action are so great that they practically prohibit its use.

As a cooling agent it produces temperatures too low for the best preservation of foods, so that liquefied ammonia gas is used instead. For other low temperatures where liquid ammonia does not produce a sufficiently low temperature liquefied carbon dioxide is usually used. (See §263.)

Liquid air is now used for removing hair from hides for tanning purposes. The hides are thoroughly dried, immersed for a minute in liquid air, drained for a few seconds, then scratched or shaved to break off the hairs while they are still frozen and brittle, leaving the roots in the hides.

83. Laws and Problems. (1) *Law of Boyle.* Under constant temperature the volume of a gas varies inversely as the pressure. $PV = P'V'$ or $V' = \frac{PV}{P'}$. P and V indicate the original pressure and volume; P' and V' indicate the change of pressure and volume. If a volume of gas under 760 mm. pressure measures 500 cc. what will be its volume under 740 mm?

$V' = \frac{.760 \times 500}{740} = 513.513 \text{ cc.}$ Normal pressure is always 760 mm. of mercury.

There are a number of variations from Boyle's law, the volumes of the gases not varying absolutely inversely as the pressure. The following table shows the number of liters filled at 0° by 2 liters of each gas when the pressure is increased from 1 atmosphere to 2 atmospheres.

Hydrogen	1 0006	Carbon dioxide	0 9931
Nitrogen	0.9996	Nitrous oxide	0.9924
Carbon monoxide	0.9995	Hydrochloric acid	0.9919
Oxygen	0 9991	Ammonia	0.9845
Nitric oxide	0 9989	Sulphur dioxide	0 9739

(2) *Law of Charles.* Under constant pressure the volume of a gas varies directly $1/273$ of its volume at 0°, for every change of 1 degree C. (See Table p. 62) This theoretically reduces the volume to 0 at -273°C , known as the *absolute zero*, but practically all gases are changed to liquids and the liquids to solids before that temperature is reached, and the law for gases ceases to apply. The law may also be stated that "the volume of a gas under constant pressure varies directly as its absolute temperature." Absolute temperature (A) is indicated by T ; Centigrade temperature by t . $T = t + 273$. Either may be used in the problems, but it must be remembered that the thermometers read in C, and the final reduction for volumetric changes must be expressed in A.

As a formula the law of Charles may be expressed in the A scale as $V' = \frac{VT'}{T}$; and in the C scale as $V' = \frac{V(273+t')}{(273+t)}$

Combining the laws of Boyle and Charles into one formula by joint variation we have $V'P'T' = VPT'$, or $V' = \frac{VPT'}{P'T'}$, in the absolute scale; the latter becoming $V' = \frac{V(273+t')P}{(273+t)P'}$ using C readings.

When the gas is measured over water P and P' become $P-a$ and $P'-a$ where a stands for the tension of water vapor at the temperature of the water. When collected over mercury P and P' become $P-m$ and $P'-m$, where m stands for the tension of the mercury vapor at the temperature of the mercury. See Tables 1 and 2 to find the tension of water and mercury vapor at the different temperatures. Normal temperature is 0°C . For accurate readings corrections should be made for the expansion of the barometer scale, the latitude and altitude. See Tables 3, 4 and 5.

If we have a volume of gas at 24° under a pressure of 750 mm. measuring 500 cc., what will be the volume at 12° and 760 mm. pressure?

$$\text{By formula, } V' = \frac{500 (273+12) 750}{(273+24) 760} = 473.48 \text{ cc.}$$

SCALE TO SHOW THE RELATION OF ABSOLUTE TEMPERATURE, CENTIGRADE TEMPERATURE AND VOLUME OF A GAS

<i>Absolute Temperature</i>	<i>Centigrade Temperature</i>	<i>Volume in cc.</i>
373	100	373
283	10	283
275	2	275
274	1	274
273	0	273
272	-1	272
271	-2	271
263	-10	263
173	-100	173
73	-200	73
0	-273	0

Problems. (1) *The Relation of Gaseous Volume to Pressure*, based upon Boyle's law.

1. The volume of a gas under 500 mm. pressure is 1000 cc. What is the volume if the pressure is increased to 750 mm.?

2. The volume of a gas under 750 mm. pressure is 498 cc. What is the volume under normal pressure?

3. The volume of a gas under 700 mm. pressure is 320 cc. What pressure will cause it to occupy 200 cc.?

4. The volume of a gas under normal pressure is 400 cc. What pressure will cause it to occupy 450 cc.?

(2) *The Relation of Gaseous Volume to Temperature*. Law of Charles.

1. The volume of a gas at 0° C. is 960 cc. What is the volume at 20° C.?

2. The volume of a gas at 20° C. is 400 cc. What is the volume at 0° C.?

3. The volume of a gas at -10°C . is 500 cc. What is the volume at 10°C ?

4. The volume of a gas at 10°C . is 480 cc. What is the volume at -10°C ?

5. The volume of a gas at 0°C . is 600 cc. At what temperature will the volume of the gas be 900 cc.?

(3) *The Relation of Gaseous Volume to Pressure and Temperature.*
Combining the Laws of Boyle and Charles.

1. The volume of a gas under normal conditions is 500 cc. What is the volume at 20°C . under 780 mm. pressure?

2. The volume of a gas at 25°C . under 740 mm. pressure is 600 cc. What is the volume under normal conditions?

3. The volume of a gas at -20°C . and under a pressure of 375 mm. is 748 cc. What is the volume under normal conditions?

4. The volume of a gas under normal conditions is 947 cc. What is its volume under 824 mm. pressure at -40°C ?

5. If the volume of a gas at 40°C under 780 mm. pressure is 900 cc. and the volume is constant at 50°C ., what is the pressure?

6. If the volume of a gas at 20°C . under 800 mm pressure is 400 cc., and the volume remains constant when the pressure is changed to 700 mm., what is the temperature?

CHAPTER V

SOLUTION AND ITS APPLICATION

84. Solution Defined. The term "solution" usually means that a powdered substance has been placed in distilled water and either shaken or heated, or both, until the solid has disappeared and the liquid is clear. It may, however, be extended to include various other processes, such as the dissolving of a solid in alcohol, or other liquid, the dissolving of a liquid in a liquid, a gas in a liquid, or several other combinations. (See Table 6.) Unless otherwise stated the term "soluble" will be applied to substances capable of dissolving in water. The substance dissolved is called the *solute*; the water or other liquid used is called the *solvent*.

85. Strength of Solutions. A dilute solution is one that contains only a very little of the dissolved substance in a relatively large proportion of the solvent. A concentrated solution contains a larger proportion of the dissolved substance, but there is no definite amount that must be present. A dilute solution may be concentrated by boiling.

86. Saturation. Solutions are said to be unsaturated, saturated, or supersaturated, according to the amount of the substance dissolved. Dilute solutions are always unsaturated, and concentrated solutions are often saturated. A saturated solution is one that contains as much as possible of the dissolved substance at the given temperature. As the temperature is raised it is often possible to dissolve more of the solid, and when this is true a solution that is saturated at 20° will be unsaturated if the temperature is raised to 30°.

When a solution is saturated at a high temperature it may sometimes be cooled down to room temperature without throwing down any of the dissolved solid. The cooled solution

is then said to be *supersaturated*. In cooling such a solution care must be taken not to allow any disturbance of the liquid, or the entrance of any dust, or part of the solid that has been dissolved will be thrown down as crystals.

The only method telling whether a solution is unsaturated, saturated or supersaturated, is to drop into the solution a crystal of the substance dissolved. If it is unsaturated more of the solid will dissolve; if it is saturated there will be no change; if it is supersaturated part of the solid will be thrown down as crystals.

Parts per Thousand. A more accurate method of stating the strength of a solution is to tell the number of grams of the solid in 1 liter (1000 cc.) of the solution. If a solution contains 20 grams of the solid in 1 liter of the solution, there would be 2 grams in 100 cc. and this means a 2% solution.

The strength of a solution is often indicated by its specific gravity. For example, an aqueous solution of sulphuric acid, having a specific gravity of 1.755 is 82% sulphuric acid by weight. This may be determined by floating a hydrometer of constant weight in a jar of the solution to be tested. (See Fig. 27.)

When the specific gravity is obtained from the scale on the stem of the hydrometer, the percentage by weight is found by reference to standard tables.

87. Color of a Solution. Many solutions are colorless, such as barium chloride, silver nitrate, ammonium sulphate, etc., or they may be colored, such as copper sulphate, potassium permanganate, or cobalt chloride. The color of the solution is usually the same as the color of the salt used, but sometimes the

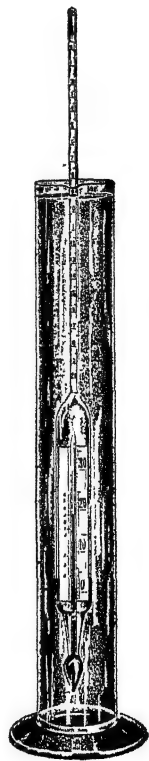


FIG. 27. Hydrometer and Jar.

color is different, as in the case of many of the aniline dyes, some of the cobalt salts, etc. Sometimes the color of a solution is so intense that it may still be visible when very dilute. Fluorescein is visible to the naked eye when one part is dissolved in 40,000,000 parts of water. If present to the extent of one part in 10,000,000 it is still so readily seen that it has been used to trace the flow of under-ground water, leakages in canals, etc.

- **88. Degree of Solubility.** Although the term "insoluble" is frequently used, it is really a relative term, since probably all substances are soluble to a slight extent if the quantity of the solvent is very large.

In approximate terms substances that are soluble in

- Less than 1 part of the solvent are called very soluble;
- From 1 to 10 parts of the solvent are called freely soluble;
- From 10 to 100 parts of the solvent are called soluble;
- From 100 to 1,000 parts of the solvent are called slightly soluble;
- From 1,000 to 10,000 parts of the solvent are called very slightly soluble;
- From 10,000 to 100,000 parts of the solvent are called nearly insoluble;
- More than 100,000 parts of the solvent are called practically insoluble.

This table does not show solubility with any accuracy. The only satisfactory method of defining solubility is to state that 100cc. of water will dissolve 24 (or some other number of) grams of the substance at 20°C (or at some other given temperature). (See Table 7.)

89. Illustration of Solubility. One of the most insoluble salts with which the student will work is barium sulphate, which requires 435,000 parts of water by weight to dissolve it, or in other words, 1 gram would require fully $3\frac{1}{2}$ barrels of water. On the other hand, 1 part by weight of water will dissolve 2.9 parts of strontium permanganate or 3.31 parts of calcium permanganate; and mercurous iodide requires 11,500 times as much water as barium sulphate.

90. Effect of Heat on Solubility. If the temperature of the solvent is raised it generally increases the degree of solubility. Potassium nitrate is about 18 times as soluble at 100° as at 0°;

and many other examples might be given. On the other hand salt is only slightly more soluble at 100° than it is at ordinary temperatures, since it requires 2.78 parts of water to dissolve 1 part of salt at 14° , and 2.48 parts at 100° . Moreover, gypsum is less soluble at 100° than it is at 0° .

91. Precipitation. An insoluble salt is often formed when two solutions are mixed. The salt will usually be thrown down as a *precipitate*. If the precipitate settles slowly it may be made to settle rapidly by use of a centrifuge. Even if there is no heavy solid formed, but merely a cloudy appearance it must be called a precipitate. If the precipitate has nearly the same specific

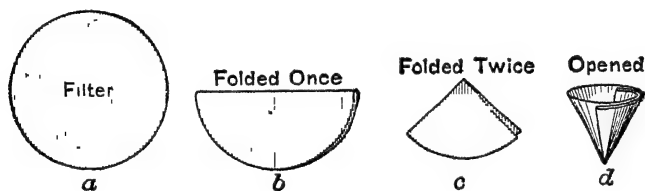


FIG 28 The Folding of a Circular Filter Paper

gravity as the liquid in the vessel the precipitate may remain rather evenly distributed throughout and is then known as a *suspension*.

The precipitate may be separated from the liquid in any one of several ways. If it settles rapidly and compactly, or if it is thrown down by the centrifuge, much of the supernatant liquid may be removed by the use of the siphon, or the liquid may be poured from the vessel, a process known as *decantation*. Most of the remaining liquid may be removed by filtration, which is usually performed by pouring the entire contents of the vessel over a folded filter paper (see Fig. 28) held in a funnel. (See Fig. 29.) The precipitate then remains upon the filter paper, and is known as a *residue*, while the liquid passes through the filter paper and is called the *filtrate*. The filtrate may contain

one or more salts in solution, and these may be recovered by crystallization.

92. Crystallization. When a solid is dissolved in a liquid, and the solution is exposed to the air, the liquid portion gradually evaporates, and the solution becomes more concentrated. At last crystals of the solid appear if the solid is one that crystallizes. Evaporation may be hastened by warming the solution, (see Fig. 30), but excessive heating usually results in the formation of a seum of small, poorly defined crystals. If the solution

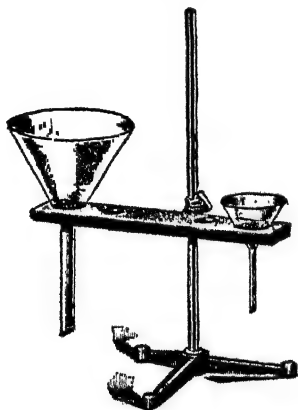


FIG. 29. Funnels Used in Filtering.

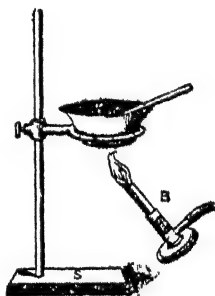


FIG. 30. Evaporating a Solution to Aid Crystallization.

is concentrated and cooled suddenly small crystals are formed; while slow cooling with slow evaporation will usually form large, well-defined crystals. (See Fig. 31.)

When substances such as sulphur, iodine or mercury are vaporized the vapor will condense upon the cool sides of the vessel at a distance from the heated section. The formation of crystals or drops in this manner is known as *sublimation*.

93. The Solution of a Gas in a Liquid. Gases dissolve in varying degrees in water or other liquids. The common hydro-

chloric acid of the laboratory and ammonium hydroxide are water solutions of the gases, hydrogen chloride and ammonia, respectively, although in the latter case there is probably a chemical combination as well.

94. Illustrations of Chemical Action in Solution. When hydrogen sulphide is passed into ammonium hydroxide, solution

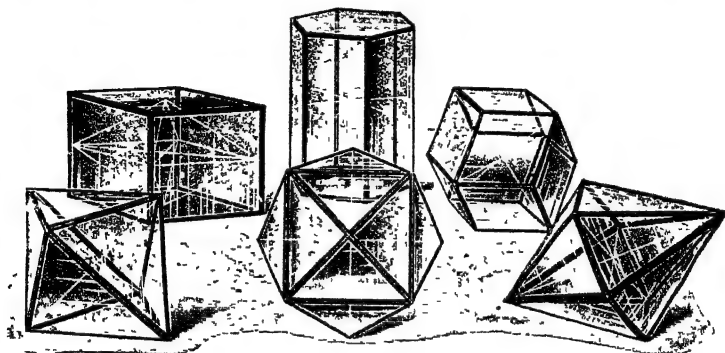
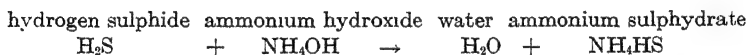
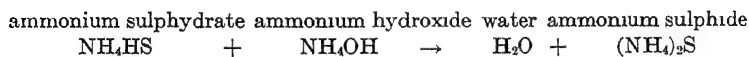


FIG 31. Some Crystal Models.

with chemical action occurs. For a saturated solution the equation is



When an equal volume of ammonium hydroxide is added to the ammonium sulphhydrate, further chemical action occurs, and we obtain the ammonium sulphide of the laboratory according to the equation



When the ammonium sulphide has stood for some time, or when sulphur is added, polysulphides of varying compositions

are formed, and these are represented by the general formula, $(\text{NH}_4)_2\text{S}_x$.

95. Temperature and the Solution of Gases. A cold liquid can invariably dissolve more of a gas than a warm liquid, since the heat causes the gas to be given off again as may be seen by heating some ammonium hydroxide. A solution of a gas in water is not the same as liquefying the gas, liquid ammonia being ammonia gas reduced to a liquid by cooling and pressure, without the presence of water.

96. Pressure and the Solution of Gases. When pressure is applied a gas will be forced into the dissolving liquid more readily. A well-known example is that of carbon dioxide, which is dissolved in water with pressure. This is used in "soda water" and when the pressure is removed the gas escapes forming bubbles.

97. Table Showing the Solubility of Certain Gases. One volume of water under the pressure of 1 atmosphere at 0° will dissolve the following common gases in the following amounts:

<i>Very soluble</i>	<i>Moderately soluble</i>	<i>Slightly Soluble</i>
Ammonia—1148 volumes	Hydrogen sulphide—4.4 volumes	Argon—0.06 volume
Hydrogen chloride—505 volumes	Chlorine—3 volumes	Oxygen—0.04 volume
Sulphur dioxide—80 volumes	Carbon dioxide—1.8 volumes	Nitrogen—0.02 volume
		Hydrogen—0.00193 volume

(See also Table 8.)

98. Solution of a Liquid in a Liquid. Liquids may dissolve in liquids, in which case either may be said to dissolve in the other. Water and alcohol may be mixed in any proportion, and will suffer a slight contraction of volume. Many other liquids may be mixed in any proportion, but some may be mixed only within certain limits, such as carboic acid, (phenol) which is soluble in 20 parts of water. Liquids which do not mix, but

which separate into layers on standing, such as kerosene and water, are called mutually insoluble.

99. The Importance of Solution in Chemical Action. Since the force that holds the elements of a molecule together can act at only short distances, chemical action is more apt to occur when the substances are brought into as close contact as possible. Of the four methods of physical division—cutting, crushing, grinding and solution—only solution can, in many instances, divide the substances so that chemical action can occur.

100. The Electrolytic Theory of Solution. Contrary to the general belief a solution is not as simple as it may at first appear. It is true that we divide the substance into exceedingly small particles, and the original substance may often be recovered when the solution is evaporated, but we find that in a solution we also have other conditions, which if properly understood will clear up a great many of the difficulties that confront the student when he begins to explain reactions. It has long been known that some solutions have the power to conduct the electric current, and are known as *electrolytes*, while others that are not able to conduct the current are known as *non-electrolytes*.

101. Conditions in an Electrolyte. Experimental evidence points to the belief that when an acid, a base, or a salt is dissolved in water a *part of the dissolved substance undergoes dissociation*, that is, it no longer exists entirely as the original substance divided into the extremely small portions, commonly known as molecules, but a *part of it has been divided into the elements, or groups of elements*, that compose the solid. Thus if common salt is dissolved in water it is not entirely common salt in the solution, but, owing to the weakening of the electrostatic force that holds the sodium and the chlorine together, it exists in the solution *partly as salt molecules, partly as dissociated sodium chloride* both the sodium and the chlorine *carrying an electrical charge*. These highly charged, dissociated portions are known as *ions*.

102. Two Kinds of Ions. Although the ions are highly charged, the solution itself is electrically neutral, so we conclude that there are two kinds of charges—positive and negative—and that the charges of opposite signs are equal. When the electric current is passed through the solution of an electrolyte the ions move to the electrodes, the positive electrode being known as the anode, and the negative electrode being known as the cathode. Since in their movement in the electrolyte the ions obey the law of magnets, that like charges repel and unlike attract, the *ions that are charged positively move toward the cathode, and are known as cations*; while the *ions that are charged negatively move toward the anode and are known as anions*. (See also §105.)

103. Distinction Between Ion and Free Element. All experiments bear out the theory that the ion is not the same as the free element. If the platinum terminals of a battery are dipped into pure water no passage of the current takes place; and if the same is tried with anhydrous hydrochloric acid the same result is obtained. On the other hand, if the two liquids are mixed, or if some of the ordinary laboratory hydrochloric acid is used, it will be found that the current passes readily through the water solution of the hydrochloric acid. (Since the chlorine set free attacks the platinum it should be replaced by carbon terminals for this experiment.) Hydrogen will appear at the cathode, or negative terminal, and chlorine at the anode, or positive terminal, in equivalent amounts, in this case equal in volume (if the gases are not collected until they have passed for some time) but the weight of the chlorine will be 35.46 times that of the hydrogen. Even if hydrogen and chlorine were composed of conducting material they could not, when distributed through a non-conducting liquid, furnish a continuous medium for the passage of the current. We are thus led to believe that the particles of hydrogen and chlorine carry charges of their own which become manifest when the hydrochloric acid is mixed with water.

104. Ionization Shown by the Centrifuge. If a solution of hydriodic acid, (hydrogen iodide) potassium iodide, sodium iodide or lithium iodide, is placed in a tube of a powerful

centrifuge (see Fig. 32) and rapidly rotated, the heavier iodide ions will be thrown to the outer end of the tube and will show a negative charge while the lighter hydrogen or metallic ions will be at the central end of the tube and will show a positive charge. Upon ceasing the rotation the liquid is at once neutral.

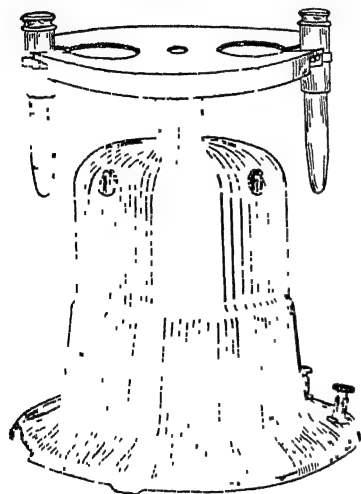


FIG. 32. An Electrically Driven Centrifuge.

105. Classification of Ions.

Various experiments all tend to show that certain substances always exhibit a positive charge while others will exhibit a negative charge. We may remember the division of the common substances

by the use of the following table:

<i>Cations, or + ions</i>	<i>Anions, or - ions</i>
All metals	Non-metals
The ammonium radical, NH_4	Acid radicals (See §155)
Hydrogen	The hydroxyl radical, OH

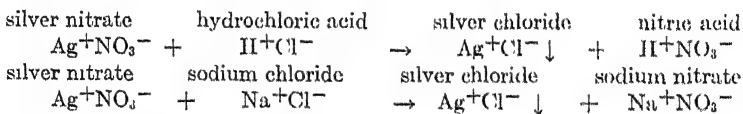
106. Symbols for Ions. In order to distinguish between the symbols for atoms and ions it is customary to write the positive ions in this manner—

H^+ , Na^+ , K^+ , Cu^{++} , Ca^{++} , Au^{+++} , Al^{+++} , Pt^{++++} etc., while the negative ions are written Cl^- , Br^- , O^- , NO_3^- , $\text{C}_2\text{H}_3\text{O}_2^-$, SO_4^- , CO_3^- ,

CrO_4^{--} , etc., or the signs may be written at the right of the ion as Cu^{++} , SO_4^{--} or $\text{SO}_4^=$, etc.

107. Degree of Ionization. In different kinds of solutions, and in different strengths of the same solution the degree of ionization differs. In solutions of salts the greater, and more active, part of the solutions is almost invariably ionic. In the case of acids and bases there is a wider range, and for the most part they are less highly ionized than the salts; but the ionized portions are more active than the undissociated molecules. The so-called "strong" acids and bases are more highly ionized than the "weak" acids and bases, that is, their solutions contain respectively a larger proportion of H and OH ions. In the second place it will usually be found that a more dilute solution will have a larger proportion of the acid, base or salt ionized than a more concentrated solution, although in the concentrated solution there may be a much larger absolute amount ionized, just as 20% of 50 is larger than 50% of 10.

108. Importance of Ionization. Since ions always act in a definite manner it is of great importance to learn how they behave in the presence of other ions. For example, the chlorine ion, Cl, will always react with the silver ion, Ag, and we can therefore, see from the following equations



that if we take *any soluble chloride we will obtain chlorine ions which will react with the silver ion from a soluble silver salt to give a precipitate of insoluble silver chloride.* Hence we may say that the formation of silver chloride is brought about by the addition of hydrochloric acid or any soluble chloride to a solution of a silver salt, thus serving as one of the tests for silver; while, conversely, if we know we have a silver salt the white precipitate is one of the tests for a chloride. Qualitative analysis

is based upon a series of such distinctive reactions. Further applications of the ionic theory to chemical reactions will be taken up in the following chapters.

109. Problems. *Simple Proportion.* Many problems in chemistry depend upon simple proportion for an easy solution

If $a=2$, $b=3$, $c=4$, and $d=6$, then

$$a \cdot b :: c : d$$

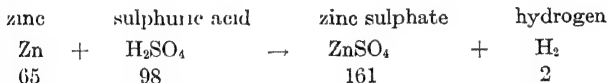
$$a \cdot c :: b : d, \text{ etc.}$$

Since a proportion consists of two equal ratios we may see from these that $\frac{a}{b} = \frac{c}{d}$ or $\frac{a}{c} = \frac{b}{d}$, and from either of these may be obtained the equation $ad=bc$.

The following method is based entirely upon proportion:

To Find the Combining Weights of the Factors and the Weights of the Products Obtained When any Amount is Used or Desired

In the equation



we say that 65 grams of zinc will react with 98 grams of sulphuric acid and give 161 grams of zinc sulphate and 2 grams of hydrogen. It is evident that if we used twice as much zinc and sulphuric acid we would obtain twice as much of the zinc sulphate and hydrogen; while if we used only half as much zinc and sulphuric acid we would obtain only half as much of the zinc sulphate and hydrogen. *No matter how much we use, therefore, we will always obtain a proportional result under the same conditions.*

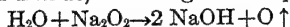
Suppose we have only 40 grams of zinc instead of 65. We may work the problem as a proportion thus,

65 : 98 :: 40 : x , the value for x giving the weight of acid required.

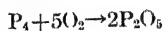
65 : 161 :: 40 : x , the value for x giving the weight of the ZnSO₄ obtained.

65 : 2 :: 40 : x , the value of x giving the weight of the hydrogen obtained. The same thing in a shorter form is found by observing that we have taken 40/65 of the weight of the zinc used in the standard equation. Therefore, we may take 40/65 of 98 to determine the amount of sulphuric acid to be used; 40/65 of 161 to determine the amount of zinc sulphate formed, and 40/65 of 2 to determine the amount of hydrogen obtained.

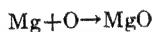
1. How much oxygen will be obtained by the action of water upon 3 grams of sodium dioxide, according to the equation



2. How much oxygen is necessary to burn 1 gram of phosphorus to phosphorus pentoxide?



3. How much oxygen is necessary to burn 1 gram of magnesium to magnesium oxide?



4. How many kilograms of calcium carbonate are required to form 10 kilograms of carbon dioxide?



CHAPTER VI

WATER AND HYDROGEN DIOXIDE

WATER. FORMULA, H_2O

110. Occurrence. Water occurs free in enormous quantities, covering about $3/4$ of the earth's surface, while it exists in the air as a vapor. In combination with other substances it occurs in many compounds, both organic and inorganic. The human body is about 70% water, and some vegetables are more than 90% water. It is estimated that about 7% of the entire earth by weight is water. Water is contained in chemical substances in three ways: (1) as water of crystallization, particularly in the sulphates and double sulphates where it sometimes is the cause of the color of the crystals, as in copper sulphate; (See also §115). (2) It may be mechanically enclosed either in the pores or between the crystals, as in granite. (3) It may be necessary for the existence of the substance as such, although it does not appear as water in the formula, and when obtained from these substances by heating, the substance loses its characteristics, as sugar, starch, dextrin, cellulose, etc. Such substances contain hydrogen and oxygen, in the proportion to form water, combined with carbon, such as cane sugar, $C_{12}H_{22}O_{11}$, which as far as the elements are concerned might be written $C_{12}.11H_2O$, but sugar cannot be made by stirring carbon in water, nor does the water exist as water of crystallization, so the first formula is used.

111. Efflorescence and Deliquescence. When a substance contains water of crystallization it may hold the water so closely combined that strong heat is required to cause the water to leave the crystal. This is the case with copper sulphate. On the other hand, such substances as sodium carbonate and sodium sulphate *hold the water of crystallization so loosely combined that*

when they are exposed to the air for a while they lose their water of crystallization and crumble to a dry powder. When a substance loses water in this way, gradually turning to a powder,

the process is known as *efflorescence*, and the substance is said to effloresce.

Deliquescence is the exact opposite of efflorescence, and the substance takes up water from the air, becomes moist, and gradually dissolves in the water absorbed. Such substances as potassium hydroxide, sodium hydroxide, calcium chloride, dehydrated copper sulphate, potassium acetate, etc., deliquesce when exposed to the air. Hence they should always be kept in closely stoppered bottles. Several of the substances which take up water readily from the air are used as drying agents in the laboratory for drying gases, the ones more commonly used being calcium chloride, calcium oxide, sulphuric acid, soda lime, etc.

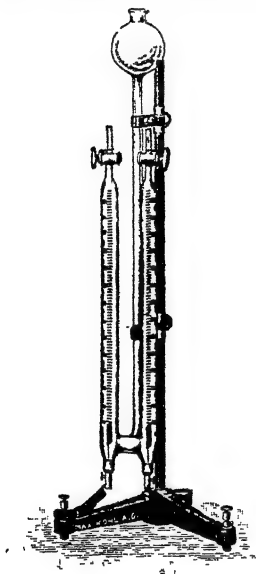


FIG. 33. Analysis of Water,
by the Electrolysis of
Dilute Sulphuric Acid.

112. Composition of Water.

When a few drops of sulphuric acid are added to water and the electric current is passed the gases formed will be found to be 2 parts of hydrogen and 1 part of oxygen by volume. (See Fig. 33.) If a mixture of 2 parts of hydrogen and 1 part of oxygen is exploded the resulting liquid will be found to be water. (See Fig. 34.)

An excess of either gas will remain uncombined, so that the composition of water is shown both by analysis and synthesis to be 2 parts of hydrogen and 1 part of oxygen by volume, and the simple formula for the molecule of water is, therefore, written H_2O .

113. Physical Properties. Pure water is tasteless and odorless, and is colorless except when seen in large masses, when the color is generally bluish or greenish, unless contaminated by some substance that colors the water otherwise.

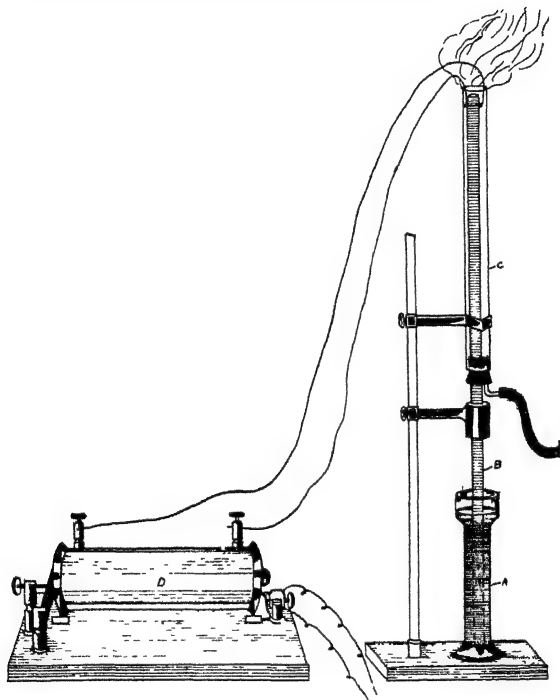


FIG. 34. Synthesis of Water

Below 0° water is a solid; between 0° and 100° it is a liquid; and above 100° it is a gas under a pressure of 1 atmosphere. An increase of the pressure raises the boiling point and lowers the freezing point. Decreasing the pressure produces the opposite effects. Illustrations of snow crystals are shown in Fig. 35.

The density of water is greatest at 4° , so that ice is lighter than water, having a specific gravity of about 0.90 where water has a specific gravity of 1 as a standard. If water continued to

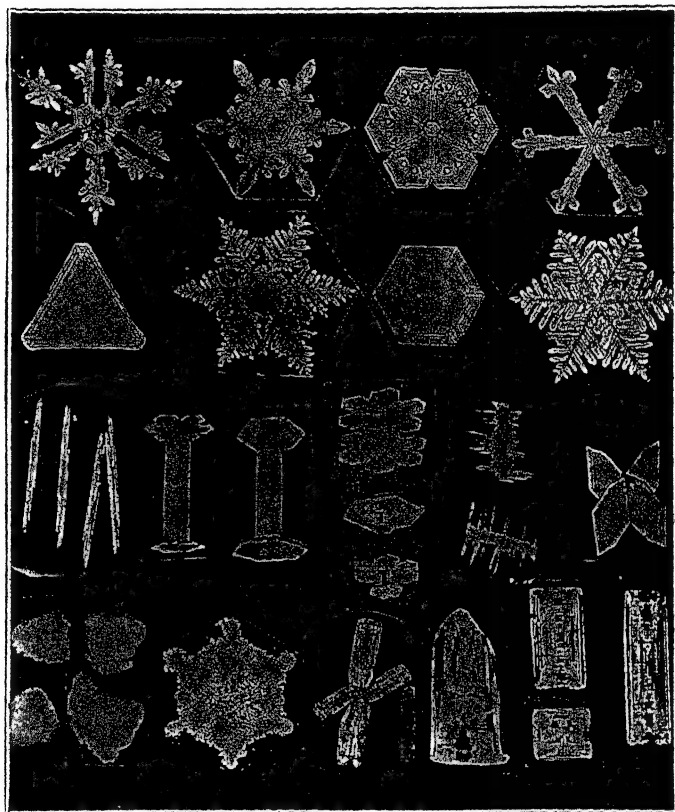


FIG. 35. Snow Crystals.

contract until it reached the solidification point, as most substances do, the denser cold water would freeze first on the bottom, instead of the surface, of a body of water, and even in a

moderately cold winter rivers, lakes and ponds would become solid bodies of ice that would never melt since ice is a poor conductor of heat. This may be shown by heating a test tube of water at the top to boiling, while the lower portion remains so cold that ice does not melt in it. Under such conditions life would shortly disappear from the earth except in places where ice never formed.

Water vaporizes at all temperatures, but more rapidly as the temperature is raised. The vapor pressure opposes the atmospheric pressure, and an allowance must be made for this when the volume of a gas is measured over water. (See §83.)

The vapor density of water is 0.623 compared with air, and 9 compared with hydrogen. The molecular weight of water is 18, as compared with the theoretical molecular weight of nearly 29 for dry air. Hence moist air is lighter than dry air.

Water is taken as the *standard of specific heat*, and accordingly the amount of heat required to raise the temperature of 1 gram of water 1 degree C. is called a *calorie*. (The large calorie, used in food analysis and in gas and coal analysis is 1000 times the small calorie.) No other single substance requires as much heat as water to produce an equal temperature change. Ice requires only 0.5 calorie to raise the temperature of 1 gram 1 degree, and steam requires only 0.47 calorie under the same conditions. On the other hand when ice changes to water 80 calories are required to melt 1 gram of ice without raising the temperature of the water; and when water changes to steam approximately 536 calories are required to change 1 gram of water to 1 gram of steam without raising the temperature. The heat that disappears without causing any rise of temperature is often called latent heat.

The amount of heat in calories required to raise the temperature of 1 gram of ice at -10° to steam at 120° may be seen from the following table:

Cal.

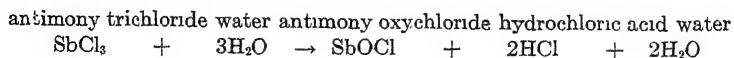
To raise the temperature of 1 gram of ice at -10° to ice at 0°	
requires $1 \times 10 \times 0.5$ calorie	5
To change the ice at 0° to water at 0° requires 1×80 calories	80
To raise the temperature of the water at 0° to water at 100°	
requires $1 \times 100 \times 1$ calorie	100
To change the water at 100° to steam at 100° requires 1×536	
calories	536
To change the steam at 100° to steam at 120° requires $1 \times 20 \times 0.47$	
calorie	9.4
Total calories	730.4

Of this amount only 114.4 calories are required to raise the temperature, while 616 calories are required to bring about the two changes of state.

The weight of 1 cc. of water at 4° C., when it has its greatest density, is called 1 gram. The freezing and boiling points of water give the fixed points of the various thermometer scales in use. (See §32.)

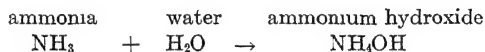
114. Chemical Properties. When a gram of hydrogen is burned in air or in oxygen to form water, fully 28,800 calories of heat are given out, and if water is to be decomposed by heat alone that amount of heat must be added for each gram of hydrogen obtained, and this heat must be concentrated so as to obtain high temperatures, since water does not begin to decompose under the influence of heat alone until a temperature of 1000° has been reached and is only partly decomposed at 2500° . If the products of the decomposition are not removed as fast as they are formed the gases recombine even at that temperature and equilibrium is established, so that no further decomposition is possible.

On the other hand a number of the active metals decompose water at ordinary temperatures, such as potassium, sodium, calcium, etc. Certain chlorides also react with water forming basic chlorides, such as



Water appears on both sides of the equation because it must be present in excess, although only one of the water molecules reacts with the trichloride.

When a gas dissolves in large amounts in water there is usually chemical action also. Thus ammonia, NH_3 , is very soluble, and when it dissolves in water the chemical action is represented by the equation



Water is necessary in nearly every chemical reaction. It serves to bring about ionization and to bring the ions into close contact with each other. (See §101 ff.) As will be explained in Chapter 8, acids, when ionized, yield hydrogen ions, while bases yield hydroxyl ions, OH . Water, H_2O , may be written H^+OH^- , but water does not ionize, since a dilute solution of water in water is impossible. Thus there are no free hydrogen or hydroxyl ions in water, and water, therefore, does not exhibit either acid or basic properties, but is neutral. Even if water ionized the proportions of hydrogen and hydroxyl would be equivalent, and would neutralize each other, producing a neutral liquid, water.

115. Water of Crystallization. Many apparently dry crystals yield water when heated. The amount of water in crystals varies from none to more than half of the weight of the crystal. The water and the other elements forming the crystal form a rather unstable compound that gives up all or part of its water when heated slightly above the temperature of boiling water. If a part of the water requires a high temperature to drive it off that part of the water is often called the water of constitution. The substance that remains after the water is driven off is called *anhydrous* or *dehydrated*.

When all of the properties of water are taken into account it is safe to say that it is the most remarkable chemical compound known. When compared with other substances, nearly every property is an extreme, usually a maximum.

The following table shows

THE PERCENTAGE OF WATER IN SOME OF THE COMMON CRYSTALS

<i>Substance</i>	<i>Formula</i>	<i>Percentage of Water</i>
Sodium carbonate	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	62.9
Sodium sulphate (Glauber's salt)	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	55.9
Magnesium sulphate (Epsom salt)	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	51.2
Aluminum sulphate	$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	48.6
Sodium tetraborate (Borax)	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	47.1
Potassium aluminum sulphate (Alum)	$\text{K}_2\text{Al}_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$	45.5
Ferrous sulphate (Green vitriol)	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	45.3
Zinc sulphate (White vitriol)	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	44.
Copper sulphate (Blue vitriol)	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	36.
Copper nitrate	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	22.4
Calcium sulphate (Gypsum)	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	20.9
Calcium sulphate (Plaster of Paris)	$(\text{CaSO}_4)_2 \cdot \text{H}_2\text{O}$	6.2
Sodium chloride (Common salt)	NaCl	0.0

116. Kinds of Water. The most important kinds of water are distilled, soft, hard and mineral. Distilled water is the purest and is obtained from the condensation of steam. (See §120.) If the water that is boiled is free from substances that volatilize at or below 100° the water that is obtained is practically pure, especially if redistilled, and should be used for all exact work in the laboratory.

Of the many varieties of natural waters, rain water as it falls, or as it is obtained from the melting of clean snow, is more like distilled water than any other. The water of the last part of the shower is purer than that of the first part.

Hard waters contain mineral substances in solution to a greater or less degree. Hard water is usually divided into two classes, (1) temporarily hard, containing carbonates in solution; and (2) permanently hard, containing sulphates in solution. The carbonates of temporarily hard water are chiefly calcium, with smaller amounts of magnesium and iron, and these may be thrown down by boiling, since they are held in solution by the presence of carbon dioxide and thus exist in the form of bicar-

bonates as $\text{Ca}(\text{HCO}_3)_2$, and the carbon dioxide is driven out by heat, forming the normal carbonate, CaCO_3 , which is insoluble. This gives rise to deposits in tea kettles, where hard water is used, and is the chief material in troublesome boiler scale. (See §401.) The removal of the carbonate, either by boiling or by chemicals softens the water. (See §782.)

117. Contamination of Water. Since water is known as the universal solvent it is difficult to keep water in a state of absolute purity. As it falls through the air the gases of and in the air

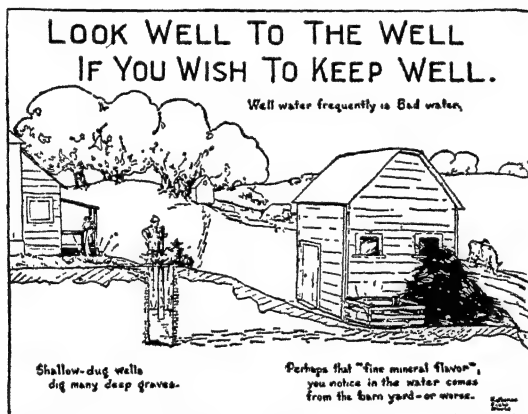


FIG 36. A Source of Impure Water.

dissolve in it to a certain extent. When it falls upon the ground the various materials with which it comes in contact dissolve in it to a greater or less degree, and the same thing occurs when the water sinks into the earth, or flows in the rivers to the lakes and oceans. Many of these substances are harmless, but others are dangerous to health and to life. The simple inorganic materials usually found in hard or mineral waters are harmless, but when water comes in contact with decaying animal and vegetable materials, or if it is contaminated by leakage from

sewers, barns and outhouses, the water becomes unfit to drink. (See Fig. 36.) Sometimes this contaminated water has a disagreeable odor and taste, but at other times it is practically odorless and tasteless, and the impurities can be detected only by examining the water both chemically and bacteriologically. (See Fig. 37.)

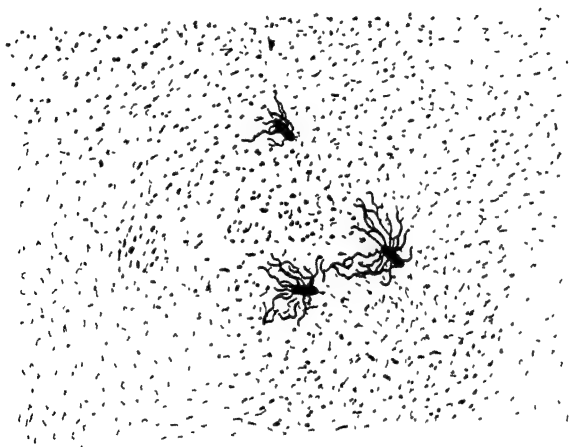


FIG. 37. Typhoid Bacilli.

Such examinations are long and are much too difficult for the beginner.

118. Sea Water and Artesian Water. The water of the oceans is said to contain somewhere in its vast extent nearly every known mineral substance in solution. Since only pure water evaporates, the mineral matter remains and as the rivers are constantly bringing more of the dissolved substances to the oceans, the water in them is gradually becoming richer in mineral matter. Sodium chloride (common salt) is the most abundant substance found in sea water, making the sea the great source of common salt.

The composition of the ocean is given by Prof. F. W. Clarke as follows:

<i>Element</i>	<i>Percentage by Weight</i>
Oxygen	85 79
Hydrogen	10 67
Chlorine	2 07
Sodium	1 14
Magnesium	0 14
Sulphur	0 09
Calcium	0 05
Potassium	0 04
Bromine	0 008
Carbon	0 002
<hr/>	
Total	100 00

The composition of the oceanic salts is given as follows:

<i>Salt</i>	<i>Percentage by Weight</i>
Sodium chloride	77 76
Magnesium chloride	10 88
Magnesium sulphate	4 74
Calcium sulphate	3 60
Potassium sulphate	2 46
Calcium carbonate	0 34
Magnesium bromide	0 22
<hr/>	
Total	100 00

The total salts have a specific gravity of approximately 2.25. If the total salts were extracted they would have a volume of approximately 4,800,000 cubic miles, or enough to cover the total surface of the United States, including all possessions to a depth of nearly 1.25 miles.

Artesian water, coming from a deep boring, is usually pure, but may contain such an abundance of mineral matter as to make the water unfit for drinking purposes. Some of the artesian water is used for medicinal purposes when it contains various salts in the right proportions. Often Epsom salt is the chief

constituent, and the same results could be obtained by taking medicinal doses of magnesium sulphate. Many bottled "mineral" waters are bottled in a factory, and are made to imitate a natural water.

Underground water charged with carbon dioxide dissolves the limestone (calcium carbonate) and when the water escapes into a cave and the pressure is removed the carbon dioxide escapes and the limestone is deposited in the form of a large icicle, known as a stalactite, or if it drops to the floor it is built up into a stalagmite.

119. Good drinking Water should have *no color nor odor*, even after standing in closed vessels for several days. Its *taste should be pleasant* but not too pronounced. It should *contain nothing that will injure the system* when taken internally, but *may contain certain solids* in solution so as to overcome the insipid taste of pure water. It *should contain the gases of the air* dissolved in it. There should be *no contamination by decaying animal or vegetable substances*, and it must be *free from harmful bacteria*.

The taste of drinking water depends upon the presence of dissolved salts chiefly of iron, manganese, magnesium, calcium, sodium and potassium which may occur as the hydroxide, nitrate, chloride, carbonate or sulphate. One part of iron or manganese may be detected in about 50,000 parts of water. If free carbon dioxide occurs in quantities greater than 100 mg. per liter, the taste is influenced so much that added salts can scarcely be noticed. The taste is influenced not only by the kind and amount of metallic salt present but differs considerably at different temperatures and is also different in different parts of the mouth.

120. Purification of Water. Drinking water may be purified in several ways. It may be boiled, distilled, aerated, filtered, or treated chemically. *Boiled water* has a flat insipid taste, disagreeable to most people. To be effective the boiling should be continued for at least a half hour. This will usually kill 99%

of all the bacteria present, and the others are almost invariably non-injurious, but they may be destroyed by boiling the water under pressure at a temperature of 115° . (See §896.)

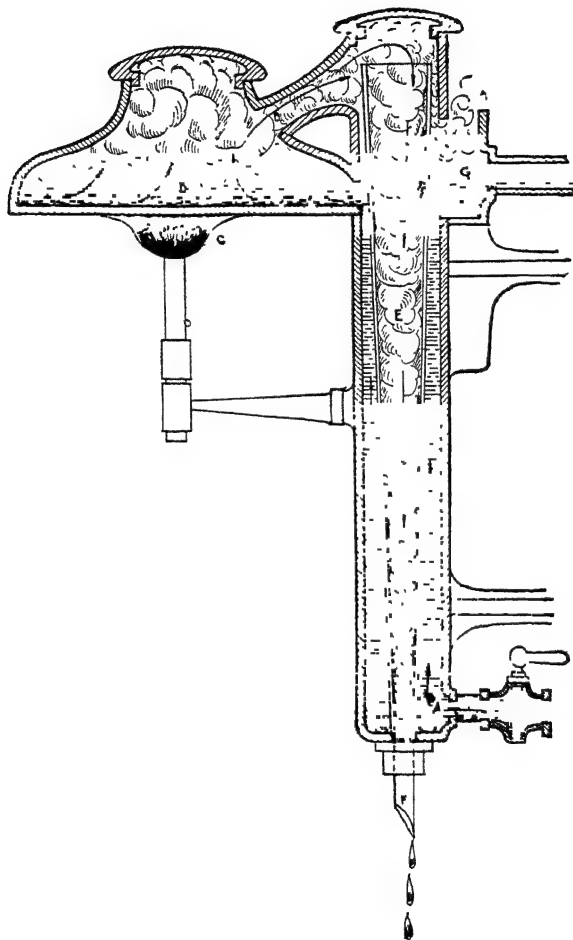


FIG. 38. Distillation of Water.

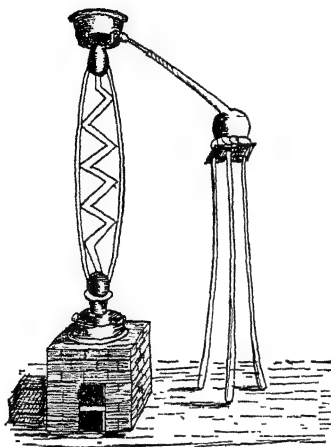


FIG. 39. An Old Still Not Using Water for Condensing the Vapors.

Distilled Water is produced by turning water into steam, and condensing the steam by allowing it to pass through a tube surrounded by cold running water. (See Figs. 38 and 39.)

Filtered water is more pleasant to the taste but is not as pure. A filter should have an extended surface where large amounts of water are used. For a cistern a very efficient filter may be made from layers of sand and gravel alternating with layers of charcoal. (See Fig. 40.)

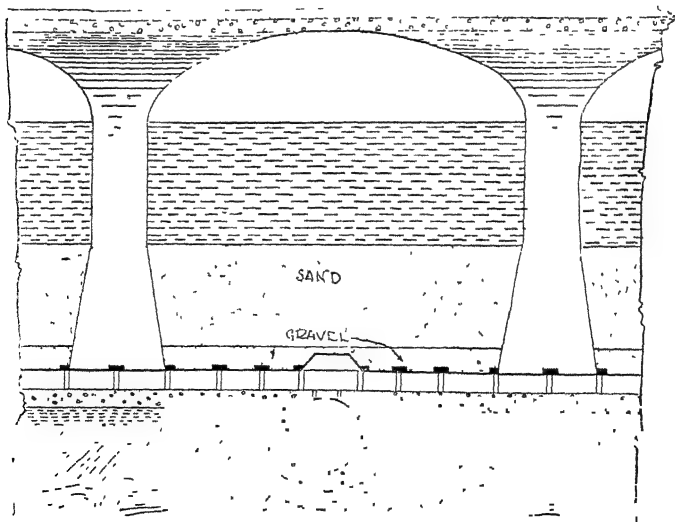


FIG. 40. A Sand and Gravel Filter.

Small amounts of suspended solid material may be separated by filtering through filter paper. This paper is nearly pure cellulose, and will retain very finely divided particles. A small household filter is illustrated in Fig. 41.

Water is often purified by the addition of certain chemicals, the exact nature of the treatment depending upon the substances to be removed. For purification of drinking water where typhoid bacilli are present chlorine is usually used. (See §222.)

Sanitary control of drinking water reduced the number of deaths from typhoid fever in Minnesota from 700 in 1910 to 82 in 1919, with the decrease in the number of cases from 14,000 to 1640. From 1900 to 1910 the average number of deaths per year was 428.

The method of purifying water in St. Louis costs \$6.71 per million gallons. The treatment consists of 0.49 grain of ferrous sulphate per gallon, 5.21 grains of calcium oxide per gallon, 0.86 grain of aluminum sulphate per gallon, and 3.07 pounds of chlorine per million gallons.

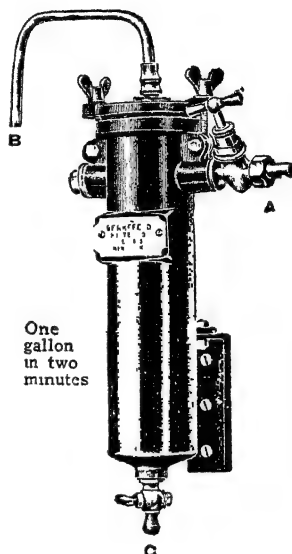
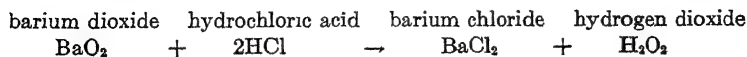


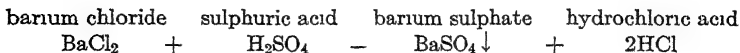
FIG. 41. A Small Household Filter.

HYDROGEN DIOXIDE, H_2O_2

121. Hydrogen dioxide, or as it is usually called, hydrogen peroxide, may be prepared when a paste made of barium dioxide and water is added to a cold dilute solution of hydrochloric acid.



By adding sulphuric acid cautiously to the mixture the barium chloride is precipitated as the sulphate and the hydrochloric acid is regenerated so that more of the paste may be added.



Finally the barium chloride may be precipitated by silver nitrate and the solution is then poured off and evaporated in a vacuum or is allowed to stand over sulphuric acid in a vacuum. Either sulphuric or phosphoric acid may be substituted for the hydrochloric acid. Hydrogen dioxide may also be made by dropping slowly two or three grams of sodium dioxide into a dilute solution of sulphuric acid (1:20). The liquid should be constantly stirred.

122. Properties. When pure, hydrogen dioxide is a colorless, odorless, syrupy liquid. Its specific gravity is 1.452. It does not become solid at -30° . It is very unstable and decomposes into water and oxygen even at ordinary temperatures when allowed to stand, and if heated rapidly to 100° an explosion is apt to occur. Since hydrogen dioxide gives off oxygen so readily it is used as an oxidizing agent, particularly in bleaching, and it finds some use in medicine. Hydrogen dioxide is sold in solutions of varying strength, usually about a 3% solution. It is bitter to the taste, and if concentrated causes a prickling sensation when applied to the skin and produces white spots. Hydrogen peroxide is sold under many names either alone or as metallic peroxides. Dioxygen contains about 3%, perhydrol about 33%. Some of the trade names are hydrozone, glycozone and pyrozone. As metallic peroxides it may be obtained as sodium peroxide (oxone), magnesium peroxide (heptogan), zinc peroxide (ektogan), etc.

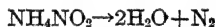
123. Chemical Action of Hydrogen Dioxide. *When hydrogen dioxide reacts with any other substance it is reduced, since it is the highest oxide of hydrogen known. The reactions are, therefore, based upon the effects upon the other substance.* In the

first class of reactions the other substance is *oxidized*, for example, lead sulphide becomes lead sulphate. In the second class the other body *undergoes no change* as when hydrogen dioxide is mixed with such substances as manganese dioxide, platinum, gold, silver, carbon, etc. In the third class of reactions the other body is *reduced*. This happens in cases where the other body is rich in oxygen, such as potassium permanganate, potassium dichromate, etc. In these cases of mutual reduction the atoms of oxygen join to form molecules of oxygen.

124. The *best test for hydrogen dioxide* is to add to the solution to be tested a little ether and a few drops of potassium dichromate solution. If hydrogen dioxide is present the dichromate is reduced to perchromic acid and upon shaking the tube this is absorbed by the ether and a blue color is produced. The ether may be omitted and the dichromate is made acid by a little sulphuric acid. If the ether is not added the perchromic acid is rapidly reduced and the solution turns green. If hydrogen dioxide is present in rain water it may be detected by this method.

125. Problems.

1. How much nitrogen is evolved from five grams of ammonium nitrite?

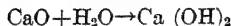


2. How many grams of ammonium chloride and how many of potassium nitrite must be used to form 10 grams of ammonium nitrite? (§70)

3. From its action upon water which will evolve more hydrogen, a gram of sodium or a gram of potassium? Show the result by a quantitative equation. (§61).

4. How much sulphuric acid will react with ten grams of each of the following metals: iron, zinc, magnesium, manganese? How much hydrogen could be obtained from each of these reactions? Would there be any difference if you used hydrochloric acid instead of sulphuric? (§59).

5. How many grams of water are required to change 25 grams of calcium oxide to calcium hydroxide?



6. How many grams of water of crystallization in 10 grams of each of the following salts: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$; $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$; $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

7. How much water can be decomposed by 5 grams of each of the following metals: sodium, potassium, calcium? (§61).

CHAPTER VII

NITROGEN COMPOUNDS

The most important compounds of nitrogen in elementary work are ammonia, nitric acid and nitrates, and the oxides of nitrogen.

AMMONIA. NH_3

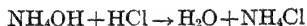
126. Occurrence. Whenever organic matter containing nitrogen decays, ammonia is formed. To a slight extent some of the ammonium compounds are found in the air, while they are often found in water. The occurrence of ammonium salts in water means contamination, probably from sewage.

127. Source and Preparation. The direct union of nitrogen and hydrogen is very difficult so that the formation of ammonia by synthesis is very seldom attempted, only 2% of the mixed gases uniting unless the ammonia is removed as fast as it is formed, otherwise equilibrium occurs and the reaction ceases. This percentage may be increased to 8 by passing the mixed gases under 200 atmospheres pressure and at a temperature of 500° over specially prepared iron or uranium, known as the Haber process. The uncombined gases may be used many times until practically entirely combined.

A contact agent for the synthesis of ammonia may consist of an alkali which has been heated in ammonia gas. The starting material may be calcium ferrocyanide, potassium ferrocyanide, or various other similar compounds made into solution. Pumice stone is immersed in the solution, the water is vaporized and the mass is given a preliminary heating to about 350° in an atmosphere of oxygen-free hydrogen or nitrogen, or in a mixture of both, or in an atmosphere of ammonia. The material is then transferred to an autoclave and heated not above 650°

in a current of ammonia gas at atmospheric pressure. The product is then capable of producing synthetic ammonia at a temperature of about 400° under a pressure of 100 atmospheres, considerably less than required by the Haber process.

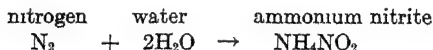
Ammonia has been obtained for a number of years *from the wash water of the gas works* where the gas is made from the distillation of bituminous coal. The ammonia dissolves in the wash water, and when different acids, such as hydrochloric, sulphuric or nitric, are added to the water containing the ammonia, salts of ammonium are obtained, according to the acid used.



These salts are the basis of the other ammonium compounds, and will give off ammonia when heated with strong caustic alkalies, such as the hydroxide of sodium, potassium or calcium.

The cokemakers of the United States permit most of the ammonia to go to waste, losing enough to make 400,000 tons of ammonium sulphate per year, although we have been importing 70,000 tons used chiefly as a source of nitrogen in fertilizers. (See Chapter 29).

Later methods derive the gas from the distillation of the refuse of packing houses, tanneries, etc. It is also formed when electric sparks are passed through nitrogen in the presence of water. Nitrous acid is formed at the same time, and this reacts with the ammonia forming ammonium nitrite, so that this compound is always formed in the air in minute quantities during electrical storms. The equation is

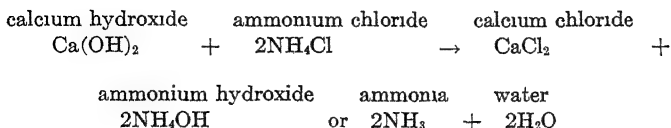


No matter how the ammonia is prepared it is usually *dissolved in water to form ammonium hydroxide*, commercially known as ammonia water or aqua ammonia. Ammonia is exceedingly soluble in water, and, as in other cases where the gas is quite

soluble, there is probably chemical reaction between it and the water. The equation is reversible



The usual laboratory method of obtaining ammonia gas is to heat a little ammonium hydroxide, collecting the gas in dry inverted receivers. It may be obtained by heating ammonium chloride or other ammonium salt with calcium hydroxide,



or by heating any ammonium salt with any strong alkali as NaOH, KOH or Ca(OH)₂. (See Fig. 42.)

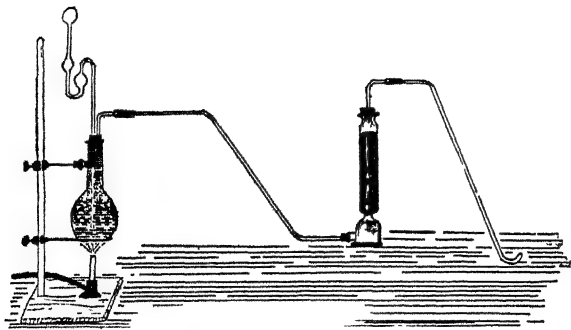


FIG. 42. Preparation of Ammonia.

Liquid ammonia may be obtained in small iron cylinders.

128. Physical Properties. Ammonia is a colorless, transparent gas, with a sharp, burning taste, and a very penetrating, overpowering odor. If breathed in large amounts suffocation results. The gas is 8.48 times as heavy as hydrogen and only

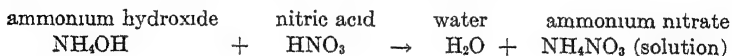
about 0.597 as heavy as air. Ammonia becomes a liquid at -40° under normal pressure, or at -10° under 6.50 atmospheres, or at ordinary temperatures by pressure alone. It turns to a white crystalline solid with very little odor at -77° . Just as any liquid in turning to a gas absorbs heat, so ammonia absorbs heat from surrounding objects when turning from the liquid to the gas and this principle is made use of in manufacturing artificial ice, (§132.)

One volume of water will absorb about 1148 volumes of ammonia gas at 0° . Since 1 cc. of water weighs 1 gram, and 1 liter of ammonia weighs 0.7706 gram it means that 1 gram of water will absorb about 0.875 gram of ammonia at 0° . The ammonium hydroxide as used in the laboratory has a specific gravity of 0.855 to 0.882 which means that at 15° it is about a 35% solution.

Ammonia is usually dried by passing it through a tower filled with calcium oxide or soda lime. Calcium chloride is not used because there is chemical action between it and the gas.

129. Chemical Properties. Ammonia will not support ordinary combustion, nor will it burn in the air, but in an atmosphere of oxygen it burns feebly with a pale yellow flame forming nitrogen and water. Like other substances, perfectly dry ammonia is very inert, not reacting to the slightest degree with perfectly dry hydrochloric acid gas, but if moisture is present the two react readily forming ammonium chloride. Ammonium hydroxide does not ionize readily and is, therefore, a weak base.

Either gaseous ammonia or ammonium hydroxide will react with acids to form ammonium salts and water, as

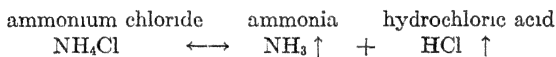


Ammonium Hydroxide, as such, has never been separated, since it always dissociates into ammonia and water. In the same way *the radical ammonium is not known in the free condi-*

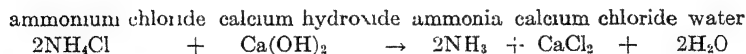
tion. When a strong solution of ammonium chloride is poured over sodium amalgam ammonium amalgam is formed, but nothing nearer the metallic ammonium has ever been formed. Ammonium hydroxide acts as a poison when swallowed. Vinegar or lemon juice acts as an antidote.

130. Composition of Ammonia. Various methods have been used for analyzing ammonia, and it may also be made by synthesis, but all methods give the same quantitative composition of ammonia, namely, 1 volume of nitrogen with 3 volumes of hydrogen or 14 parts by weight of nitrogen with 3 parts of hydrogen.

131. Dissociation of Ammonium Compounds. Ammonium hydroxide decomposes into ammonia and water if the temperature is raised only a few degrees, but the temperature required for the other compounds is considerably higher. Ammonium chloride decomposes at about 350°. The equation is



which shows that the reaction is reversible and the two gases recombine to form the original salt. This is typical of a large number of cases where the products are gaseous, but if the chloride is heated with calcium hydroxide, the hydrochloric acid, formed when the ammonium chloride is decomposed, reacts with the calcium hydroxide to form water and calcium chloride according to the regular law of neutralization, so that the final equation may be written



Other ammonium compounds that dissociate into compounds not entirely gaseous, do not have the tendency to recombine.

132. Uses of Ammonia. *Artificial Ice.* Ammonia is used very largely in artificial ice plants. The ammonia is compressed

to a liquid and is cooled under pressure by running water. (See Fig. 43.) It is then conducted through pipes placed in the brine vats where the ammonia expands to the gaseous condi-

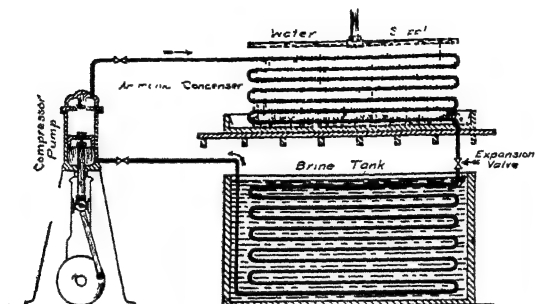


FIG. 43. Compression System for Manufacturing Ice.

tion. One gram of liquid ammonia requires 260 calories of heat to vaporize it and this heat is taken from the brine which in

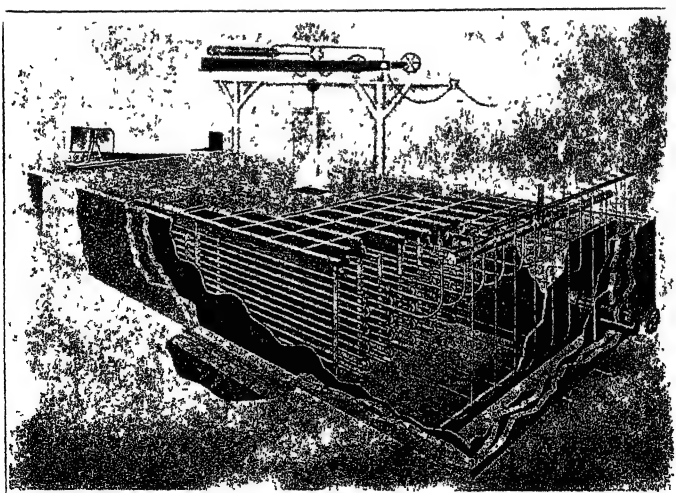


FIG. 44. Triumph Ice Tank.

turn takes heat from the water to be frozen, contained in tanks holding about 300 pounds. The ice is solid in from 36 to 40 hours. Since 1 gram of water in cooling 1 degree gives off 1 calorie of heat, and in solidifying gives off 80 calories it may readily be seen that theoretically 1 gram of liquid ammonia turning to the vapor requires the heat given off by 2.6 grams of water cooled from 20° to the point of solidification. (See Fig. 44.)

By using the same general method, but omitting the brine and the vats, ammonia is used for cooling rooms, refrigerators, etc.

Ammonium hydroxide is frequently used in the home for various purposes, such as cleaning, or for softening water. It is often, but erroneously, called liquid ammonia.

Ammonia may be used to restore consciousness in overdoses of anesthetics, or in faintness: it overcomes to a large extent the effect of chlorine, bromine vapor, sulphur dioxide, hydrochloric acid, etc., when inhaled in the laboratory; and may remove the red spots from the clothing when sulphuric or hydrochloric acid is spilled; but should not be used with the yellow

spots of nitric acid, which are permanent and become more intense in color when ammonia is applied.

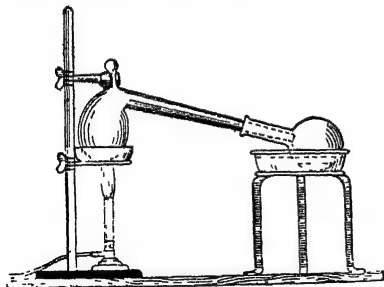


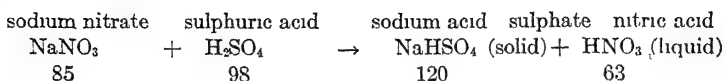
FIG. 45. Preparation of Nitric Acid.

NITRIC ACID, HNO_3

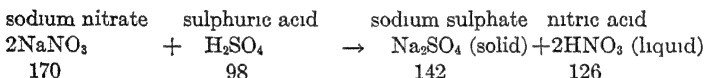
133. Source and Preparation. Nitric acid, known for nearly 1200 years, is prepared by heating sodium nitrate with sulphuric acid.

(Fig. 45.) If the temperature is moderate and gram equivalents of the reacting substances are used the resulting products are sodium acid sulphate and nitric acid, since only 1 of the

replaceable hydrogen atoms of the sulphuric acid reacts with a nitrate radical.



But if double the amount of the sodium nitrate is used and the temperature is raised the normal sulphate of sodium is formed and there will be twice the amount of nitric acid formed:



Probably the reaction occurs in two stages the first being represented by the first equation while the second stage may be

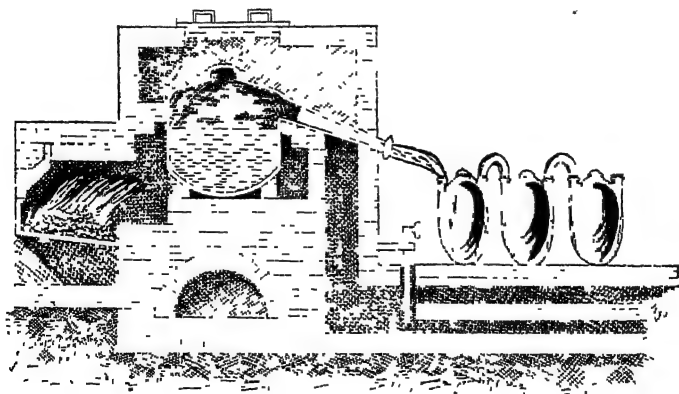
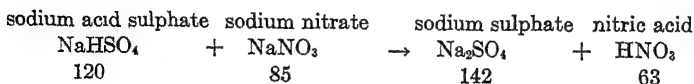


FIG. 46. Commercial Preparation of Nitric Acid.

represented by the reaction between the sodium nitrate and the sodium acid sulphate,

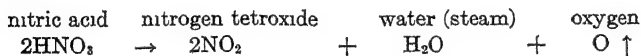


Part of the nitric acid is decomposed by the high temperature required and the acid is colored brown because of the presence of the oxides of nitrogen, forming in part fuming nitric acid so that it must be purified before being used. In commerce nitric acid is made in cast iron retorts and the pressure is reduced so as to lower the boiling point and thus prevent decomposition. (See Fig. 46.)

Sodium nitrate is a natural product and is often called Chile saltpeter to distinguish it from potassium nitrate, called salt-peter. Nitrates are formed in nature by the fixation of atmospheric nitrogen through the action of nitrifying bacteria. Artificial nitrates are now being produced. (See Chapter 29.)

134. Physical Properties. Nitric acid is a colorless, volatile liquid, boiling at 86° . It mixes in all proportions with water, and if heated when either concentrated or dilute, either water or acid will boil off until the solution is about 68% acid, with a constant boiling point at 120.5° . (See also §225, hydrochloric acid.) The purest acid usually contains some impurities such as sulphuric acid, hydrochloric acid, chlorine, etc., and is never obtained with a purity of much more than 99.5%. The specific gravity of the purest acids varies from 1.52 to 1.56, but an acid of the usual laboratory grade will have a specific gravity of about 1.42.

135. Chemical Properties. Nitric acid is very highly ionized, and is, therefore, classed as one of the strong acids. When it begins to boil at 86° it also begins to decompose, and the decomposition is complete at 256° , the reaction being represented by the equation,

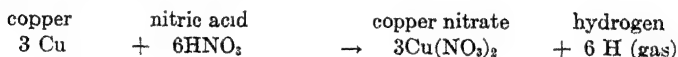


Nitric acid has two great functions, (1) it forms the nitrates of metals; (2) it acts as a powerful oxidizing agent.

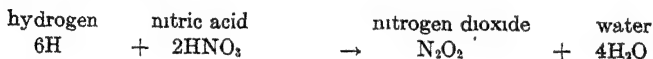
As examples of the first function we may notice the formation of nitrates from the action of nitric acid upon the hydroxides

of metals as given under neutralization, (§153). It also forms the nitrates of metals by acting upon the metals themselves, but the action is different from the action of the metals with either sulphuric or hydrochloric acid. With the last two free hydrogen will be evolved, but when nitric acid is used the nascent hydrogen acts upon the remaining acid and decomposes it, the exact products of the decomposition depending upon (1) the metal used; (2) the strength of the acid; (3) the temperature; (4) the amount of the nitrate of the metal already formed. Water will be formed together with one of the oxides of nitrogen; or water with ammonia; etc.

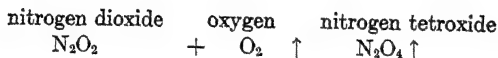
As a typical equation for the reaction of nitric acid upon a metal we may notice what occurs when a moderately concentrated acid acts upon copper.



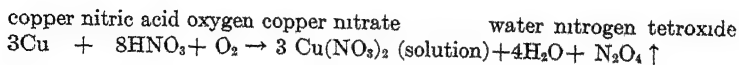
The ionic hydrogen instead of passing off as a gas, acts upon more of the acid



and the nitrogen dioxide reacts with the oxygen of the air to form the tetroxide

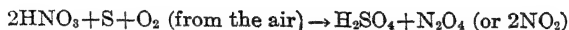


If we add the three equations together, cancelling what occurs on both sides, the complete equation might be written



If the reaction occurs in a closed vessel the reaction represented by the third equation ceases as soon as the air in the vessel has been used to oxidize the dioxide.

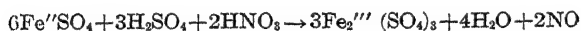
The second function of nitric acid—oxidation—is seen when substances like sulphur, phosphorus, carbon, arsenic, silicon, etc., are placed in the acid. They do not have the power of the metals to set hydrogen free but they are oxidized to the corresponding acid.



Dilute acid does not have the same oxidizing power as the concentrated acid.

Ordinary nitric acid spilled upon the skin and immediately washed off does not usually burn, but the concentrated acid will often cause painful blisters before the acid is removed. The protein of the skin reacts with the acid and the skin is colored yellow, the color remaining for about two weeks. There is no satisfactory method of removing the color. When taken internally $\frac{1}{4}$ to $\frac{1}{2}$ ounce will cause death within 24 hours.

To test for nitric acid or nitrates, add fresh ferrous sulphate solution to the solution to be tested. Incline the test tube, and let some concentrated sulphuric acid run down the tube to the bottom. A brown ring where liquids meet shows nitrates.



The brown color is caused by the formation of $\text{FeSO}_4 \cdot \text{NO}$. The color disappears when the concentration of HNO_3 increases causing a change of Fe'' to Fe''' .

Nitric acid is monobasic and forms one series of soluble nitrates, but when the acid acts with such bases as bismuth hydroxide, $\text{Bi}(\text{OH})_3$, which is a triacid base, basic nitrates of bismuth may be formed, one of which may be written $\text{Bi}(\text{OH})_2\text{NO}_3$, which may be regarded as normal bismuth hydroxide $\frac{1}{3}$ neutralized. If the hydroxide is $\frac{2}{3}$ neutralized the resulting compound is $\text{BiOH}(\text{NO}_3)_2$. If fully neutralized it is $\text{Bi}(\text{NO}_3)_3$. When $\text{Bi}(\text{OH})_2\text{NO}_3$ is heated water is given off and BiONO_3 is formed.

136. Uses of Nitric Acid. Nitric acid is very widely used, finding application in the manufacture of sulphuric acid; oxalic acid from starch, sugar, etc.; picric acid; nitro-glycerin; TNT; TNA; TNX; (§947) etching on copper and steel, refining gold, silver and other metals, etc. Mixed with hydrochloric acid (1.3) it forms aqua regia, which reacts with gold and platinum.

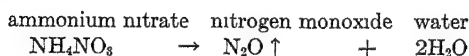
OXIDES OF NITROGEN

137. The Oxides of Nitrogen are Five in Number, differing from each other in composition and properties. Each of the compounds may be said to be made up of 2 atoms of nitrogen with varying amounts of oxygen, the amount of the variation being from 1 to 5 atoms.

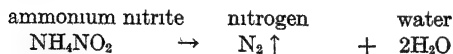
NITROGEN MONOXIDE OR NITROUS OXIDE, N_2O

138. Nitrogen Monoxide or "laughing gas," so named because of the peculiar intoxicating effect produced when a small amount of the impure gas is taken into the lungs, is used in a pure condition as an anesthetic. If the effect is to last more than a few seconds the gas is administered continuously, together with pure oxygen, and the anesthesia disappears as soon as the nitrogen monoxide is shut off and only the oxygen is given.

139. Preparation. The usual method of preparing nitrogen monoxide is to heat ammonium nitrate to 170° . (See Fig. 47.) The nitrate is decomposed by heat, and in the rearrangement of atoms the hydrogen unites with a part of the oxygen, while the remainder of the oxygen unites with the nitrogen, giving a final reaction that may be expressed by the equation



This reaction is similar to the one obtained when ammonium nitrite is heated to obtain nitrogen where the equation is



the only difference being the 1 atom of oxygen that combines with the nitrogen in the nitrate reaction. It may be purified for use as an anesthetic by passing it successively through solutions of potassium permanganate, 10% sodium hydroxide and 20% sulphuric acid.

140. Physical Properties. Nitrogen monoxide is a colorless gas having a sweetish taste and odor. Its specific gravity is 1.5298. One liter of the gas weighs 1.9777 grams. One volume of cold water will dissolve about 1.3 volumes of nitrogen monoxide. At a temperature of 0° under 30 atmospheres pres-

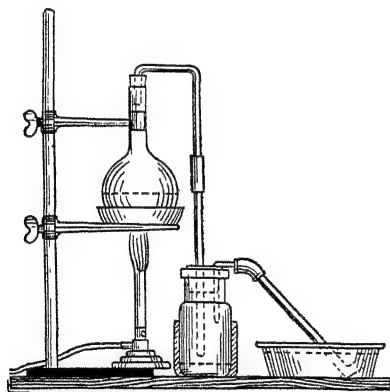


FIG. 47. Preparation of Nitrous Oxide.

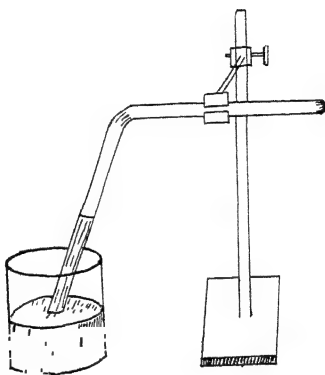


FIG. 48. Analysis of Nitrous Oxide.

sure the gas liquefies. In this condition it is sold in strong steel cylinders to doctors and dentists as an anesthetic. The liquid boils at -90° and becomes solid at -102.3° .

141. Chemical Properties. Nitrogen monoxide supports combustion about as well as oxygen, and with certain substances, as hydrogen and carbon, the combustion is even more brilliant. In order to support combustion, the gas must be decomposed, so that the free oxygen may unite with the substance to be burned. Nitrogen monoxide will even light a splinter of wood

with a spark on it, (compare with oxygen) and in this way differs from all the other oxides of nitrogen. The best way of distinguishing the gas from oxygen is to mix some of it with some nitrogen dioxide. If the gas is oxygen red fumes of nitrogen tetroxide are produced, but if it is the monoxide no change of color occurs. The gas has no effect on litmus. By placing a small piece of sodium in the horizontal arm of a bent tube filled with nitrous oxide, dipping the open end of the tube into mercury and heating the sodium, a chemical action occurs between the sodium and the oxygen of the nitrous oxide, and mercury rises in the tube until it fills $\frac{1}{3}$ of the entire tube. (See Fig. 48.) This shows that the gas is $\frac{1}{3}$ oxygen. The gas filling the remaining $\frac{2}{3}$ of the tube may be shown to be nitrogen. How?

NITROGEN DIOXIDE OR NITRIC OXIDE, N_2O_2 OR NO

142. Preparation. Nitrogen dioxide may be made by adding copper to nitric acid having a specific gravity of about 1.12. If the reaction is carried out in a flask fitted with a stopper and delivery-tube, it will be observed that red vapors of nitrogen tetroxide fill the flask at first, and then disappear as the oxygen of the air in the flask is exhausted. The oxygen has combined with the nitrogen dioxide to form the tetroxide. If the operation is carried out in the open air the constant change of air will change all of the nitrogen dioxide to the tetroxide.

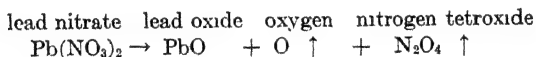
143. Physical Properties. Nitrogen dioxide is a colorless gas. Its odor is unknown, since it will unite with the oxygen of the air to form the tetroxide before one is able to smell it. Water will dissolve $\frac{1}{20}$ its volume of nitrogen dioxide. By cold and pressure, it may be condensed to a colorless liquid that boils at -142.4° and is solid at -160° . Its specific gravity is 1.0367 (air = 1). The weight of one liter of the gas is 1.34 grams.

144. Chemical Properties. Nitrogen dioxide combines directly with free oxygen to form the tetroxide, and a considerable amount of heat is evolved during the combination. If the

temperature is not too high some nitrogen trioxide is also formed. The combination of the oxygen and nitrogen is closer than in nitrogen monoxide so that the gas is not as good a supporter of combustion. Well-lighted phosphorus or magnesium introduced into the gas will burn brightly. A few drops of carbon disulphide in a bottle of nitrogen dioxide, when vaporized, will burn with a brilliant flash. Burning hydrogen will decompose the gas forming water, and set nitrogen free.

NITROGEN TETROXIDE, N_2O_4 OR NO_2

145. Preparation. If the liquid substance is desired the best method is to heat to redness, lead nitrate, $Pb(NO_3)_2$, that has been well dried. The equation for the final reaction is

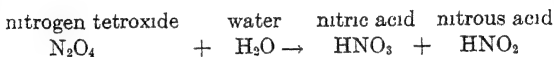


If the receiving vessel is surrounded by a mixture of ice and salt or snow and salt, a nearly colorless or yellowish liquid will form, that becomes solid at $-10\frac{1}{2}^\circ$. It may be prepared in the gaseous state by simply exposing nitrogen dioxide to the air, or to oxygen.

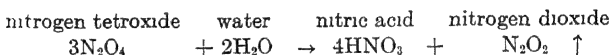
146. Physical Properties. Below $-10\frac{1}{2}^\circ$ nitrogen tetroxide is a white solid. Above that temperature it is a very pale yellow liquid that becomes darker at 0° , is orange brown at 15° , boils at 22° , giving off red brown vapors that become more intense in color until 140° is reached when they are red-black. At 600° the vapor again becomes colorless. The specific gravity of the liquid is 1.45 ($H_2O=1$). At the lowest temperatures the molecular weight is 92 and the density is 46 ($H=1$) which corresponds to the formula N_2O_4 . Above 150° the molecular weight is 46 and the density only 23 corresponding to the formula NO_2 . Between these limits both substances seem to be mixed together owing to the dissociation of part of the tetroxide when heated. The change from N_2O_4 to NO_2 is gradual. For convenience of

comparison the student should use the formula N_2O_4 at ordinary temperatures.

147. Chemical Properties. The gas is a corrosive poison and very dangerous to inhale. It acts energetically upon substances that can take up oxygen. When treated with a little cold water it decomposes into nitric and nitrous acids.



If the water is hot the reaction gives nitric acid and nitrogen dioxide.

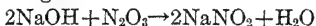


The dioxide will take oxygen from the air and again form the tetroxide. Copper, nickel and cobalt absorb the tetroxide, forming the nitro metals such as Cu_2NO_2 , a dark red powder that is decomposed at 90° into copper and nitrogen tetroxide.

Nitrogen tetroxide has been widely used in the bleaching of flour. It is illegal to use it for this purpose, since second and third grade flour may be made to resemble the finest patent flour. The method is very rapid and produces in a short time the same bleaching effect that is produced in about 3 months when it is not used.

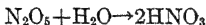
148. Problems. 1. How many grams of ammonium nitrate are required to prepare 10 liters of nitrogen monoxide? (§139).

2. Write the quantitative equation for the reaction of sodium hydroxide and nitrogen trioxide.



3. Write the quantitative equation to show the formation of nitrogen tetroxide from lead nitrate. (§145)

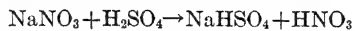
4. How much nitric acid will be formed if 20 grams of nitrogen pentoxide are added to water?



5. How much ammonia is formed by the action of 25 grams of ammonium? (§131).

6. How much hydrochloric acid is required to neutralize the ammonia formed in the preceding problem? (§127).

7. How much nitric acid can be made from one kilogram of sodium nitrate?



8. Write the quantitative equation for the decomposition of nitric acid by copper. (§135).

CHAPTER VIII

ACIDS, BASES AND SALTS

149. The Old Theory of Acids held that oxygen was the most important element in all acids, which led to numerous errors, such as supposing that hydrochloric acid, HCl , must contain oxygen. This theory has long been abandoned, but in commerce the old names still cling to many substances that are more properly called oxides, or acid anhydrides, since they give the solution of an acid when water is added. Carbon dioxide is thus often called carbonic acid, or carbonic acid gas; arsenic trioxide is called arsenious acid, etc.

150. Present Theory of Acids. Chemically an acid consists of hydrogen joined to a nonmetallic element or radical, such as HCl , HNO_3 , or H_2SO_4 . A soluble acid usually has a sour taste, turns litmus and other vegetable colors red, removes the color from reddened phenolphthalein, and is capable of reacting with a base to form water and some kind of salt, depending upon the acid and base used. The student is apt to think of all acids as liquid, because he has poured the common acids or their solutions from bottles, but a careful study of acids will show that of about 300 well defined acids, 1% are gases, 16% are liquids, and 83% are solids. Hydrochloric is the only common gaseous acid, usually used as a solution in water; nitric and sulphuric are the common liquid acids, and the others used by the beginner are solutions of solids.

151. Bases. A base-forming element is one that will unite with oxygen or the radical OH , to form a compound that will, in solution, turn red litmus blue, or colorless phenolphthalein red. The ammonium radical, NH_4 , may take the place of the base-forming element in the compound. A base will react with an acid to form water and a salt. Bases are often called hy-

form a salt. For accurate work carefully graduated burettes are used. (See Fig. 49.) If a whole number of cc. of either acid or alkali is to be taken it may be measured with a pipette. (See Fig. 50.) Care must be taken not to draw any of the liquid into the mouth.

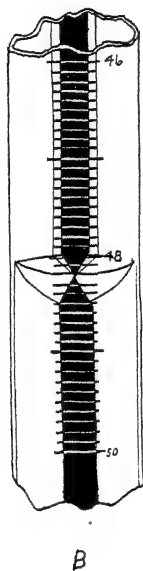
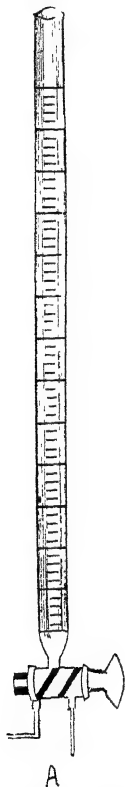


FIG. 50.
Pipettes.

FIG. 49. Burette and Section Showing
Meniscus.

154. Acid Radicals. A radical may be defined as a group of *two or more elements that usually act as a single element.* In all

discussion of the ionic theory a single element classed as a non-metal may be considered as a radical, but we shall treat a radical as a group for the present. In what may be called "test-tube reactions" the radical usually does not change either by giving up a part of itself to something else or by taking other elements from other substances. *Most radicals unite with hydrogen to form acids or with metals to form salts.* In either case the group forming the radical is the same.

155. Valence of Radicals. The *free valence* of radicals is the same as the valence of elements. Thus we have univalent radicals, having a valence of one; bivalent radicals, having a valence of two; trivalent radicals, having a valence of three; and quadrivalent radicals having a valence of four. In the list of common radicals that follows it will be noticed that in the radicals acting as non-metals oxygen is usually combined with some other element. The valence of the element combined with oxygen will be discussed in Chapter 9.

LIST OF COMMON RADICALS

The student is to *learn* first the radicals marked **; then the radicals marked *; later as many as time permits of the others.

1. Univalent Radicals.

a. Acting as a *metal*, having 1^+ charge.

$^{+}\text{NH}_4$ giving ammonium compounds, as ammonium chloride, NH_4Cl .

b. Acting as *non-metals*, having 1^- charge.

NO_2^- , giving nitrous acid, HNO_2 , or nitrites, as sodium nitrite, NaNO_2 .

NO_3^- , giving nitric acid, HNO_3 , or nitrates, as sodium nitrate, NaNO_3 .

ClO^- , giving hypochlorous acid, HClO , or hypochlorites, as sodium hypochlorite, NaClO .

- ClO_2^- , giving chlorous acid, HClO_2 , or chlorites, as sodium chlorite, NaClO_2 .
- ClO_3^- , giving chloric acid, HClO_3 , or chlorates, as sodium chlorate, NaClO_3 .
- ClO_4^- , giving perchloric acid, HClO_4 , or perchlorates, as sodium perchlorate, NaClO_4 .
- BrO_3^- , giving bromic acid, HBrO_3 , or bromates, as sodium bromate, NaBrO_3 .
- IO_3^- , giving iodic acid, HIO_3 , or iodates, as sodium iodate, NaIO_3 .
- * $\text{C}_2\text{H}_3\text{O}_2^-$, giving acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$, or acetates, as sodium acetate, $\text{NaC}_2\text{H}_3\text{O}_2$.
- MnO_4^- , giving permanganic acid, HMnO_4 , or permanganates, as sodium permanganate, NaMnO_4 .
- c. Modifications of bivalent radicals, acting as univalent, having 1^- charge.
- * $\text{HC}_4\text{H}_4\text{O}_6^-$, giving tartaric acid, $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$, or bitartrates, as sodium bitartrate, $\text{NaHC}_4\text{H}_4\text{O}_6$.
- * HCO_3^- , giving carbonic acid, H_2CO_3 , or bicarbonates, as sodium bicarbonate, NaHCO_3 .
- * HSO_4^- , giving sulphuric acid, H_2SO_4 , or bisulphates, as sodium bisulphate, NaHSO_4 .
- d. Univalent radical not forming an acid, having 1^- charge.
- ** OH^- , giving water, HOH or H_2O , or hydroxides, as sodium hydroxide, NaOH .
2. Bivalent radicals, acting as non-metals, having 2^- charges.
- SO_3^{2-} , giving sulphurous acid, H_2SO_3 , or sulphites, as sodium sulphite, Na_2SO_3 .
- ** SO_4^{2-} , giving sulphuric acid, H_2SO_4 , or sulphates, as sodium sulphate, Na_2SO_4 .
- ** CO_3^{2-} , giving carbonic acid, H_2CO_3 , or carbonates, as sodium carbonate, Na_2CO_3 .

$\bar{\text{C}}_2\bar{\text{O}}_4$, giving oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$, or oxalates, as sodium oxalate, $\text{Na}_2\text{C}_2\text{O}_4$.

$\text{C}_4\bar{\text{H}}_4\bar{\text{O}}_6$, giving tartaric acid, $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$, or tartrates, as sodium tartrate, $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$.

$\bar{\text{B}}_4\bar{\text{O}}_7$, giving tetraboric acid, $\text{H}_2\text{B}_4\text{O}_7$, or tetraborates, as sodium tetraborate, $\text{Na}_2\text{B}_4\text{O}_7$.

$\bar{\text{Cr}}\bar{\text{O}}_4$, giving chromic acid, H_2CrO_4 , or chromates, as sodium chromate, Na_2CrO_4 .

$\bar{\text{Cr}}_2\bar{\text{O}}_7$, giving dichromic acid, $\text{H}_2\text{Cr}_2\text{O}_7$, or dichromates, as sodium dichromate, $\text{Na}_2\text{Cr}_2\text{O}_7$.

$\bar{\text{Mn}}\bar{\text{O}}_4$, giving manganic acid, H_2MnO_4 , or manganates, as sodium manganate, Na_2MnO_4 .

$\bar{\text{Si}}\bar{\text{O}}_3$, giving silicic acid, H_2SiO_3 , or silicates, as sodium silicate, Na_2SiO_3 .

3. Trivalent radicals, acting as non-metals, having 3^- charges.

$\bar{\text{As}}\bar{\text{O}}_4$, giving arsenic acid, H_3AsO_4 , or arsenates, as sodium arsenate, Na_2HASO_4 .

$\bar{\text{P}}\bar{\text{O}}_4$, giving phosphoric acid, H_3PO_4 , or phosphates, as sodium phosphate, Na_3PO_4 .

4. Acid radicals, not containing oxygen.

a. Univalent, having 1^- charge.

$\bar{\text{CN}}$, giving hydrocyanic acid, HCN , or cyanides, as sodium cyanide, NaCN .

$\bar{\text{SCN}}$, giving sulphocyanic acid, HSCN , or sulphocyanates, as sodium sulphocyanate, NaSCN .

b. Trivalent, having 3^- charges.

$\bar{\text{Fe}}'''\bar{(\text{CN})}_6$, giving hydroferricyanic acid, $\text{H}_3\text{Fe}'''(\text{CN})_6$, or ferricyanides, as sodium ferricyanide, $\text{Na}_3\text{Fe}'''(\text{CN})_6$.

c. Quadrivalent, having 4^- charges.

$\bar{\text{Fe}}''\bar{(\text{CN})}_6$, giving hydroferrocyanic acid, $\text{H}_4\text{Fe}''(\text{CN})_6$,

or ferrocyanides, as sodium ferrocyanide, $\text{Na}_4\text{Fe}''(\text{CN})_6$.

In the illustrations of salts, given in the preceding list, sodium salts have been listed throughout, so that the student may concentrate his attention upon the radical, rather than upon the metal with which the radical is combined.

Among the carbon compounds there are a great many radicals, some acting as metals, others as non-metals, but they will not be discussed at this time.

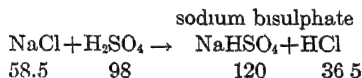
156. Salts. A salt is a combination of a metal or metallic radical with a non-metallic element or radical. Salts are formed in several ways, one of which is *the neutralization of a base by an acid*, and for practical purposes it is convenient to consider all salts as made in that manner, even when the actual formation is brought about otherwise. Salts differ from both acids and bases in that the salt is *usually neutral* towards indicators, such as litmus. The reason for this is that the *positive and negative ions are equal, and neither hydrogen ions, giving an acid reaction, nor hydroxyl ions, giving an alkaline reaction, are present in excess.* (See, however, §162.)

157. Conditions in the Solutions That Form Salts. When an acid is made into dilute solution free hydrogen cations and free radical anions are separated from the acid. In the same way in the solution of the base, free metal cations and free hydroxyl anions occur. The hydrogen and hydroxyl ions unite to form water, and the metallic cation unites with the radical anion to form the salt. As the solution is slowly evaporated the percentage of ionization decreases and the salt will appear as crystals.

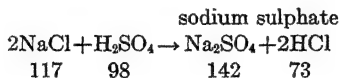
158. Classification of Acids. From the standpoint of the ionic theory acids may be divided into several classes, the division being based upon the number of *hydrogen ions set free when a molecule of the acid is dissolved in water.* Hydrochloric acid, HCl , acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$, nitric acid, HNO_3 , and other acids

containing only one atom of hydrogen outside of the radical, will yield one hydrogen ion when the acid is dissolved, and are called *monobasic*, because the one hydrogen ion can combine with only one hydroxyl radical. In the same manner sulphuric acid, H_2SO_4 , and other acids made up of two atoms of hydrogen combined with a bivalent radical are known as *dibasic acids*, because they can yield two hydrogen ions to combine with two hydroxyl radicals. Tribasic acids can yield three hydrogen ions, while tetrabasic acids yield four.

159. Replaceable or Ionizable Hydrogen. The ions of hydrogen set free in solutions of the various acids are also known as *replaceable or ionizable hydrogen*, because certain metals can replace the hydrogen in dilute acids, setting the hydrogen free in the ionic condition. Certain salts will also act upon acids and the result is very similar to the action of acids. In all these cases, however, we find that when we use a monobasic acid we are able to produce only one series of salts, and we have only sodium nitrate, or sodium acetate; but when we use a dibasic acid we may replace either one or two atoms of hydrogen, and the resulting salts will differ. Thus we may have the action of sodium chloride and sulphuric acid:



Or we may double the amount of salt used and increase the temperature and obtain the following:



The Na_2SO_4 is known as normal sodium sulphate, and the NaHSO_4 is called acid sodium sulphate, or sodium bisulphate, the latter name being given because the proportion of the SO_4 to the metal is twice as great in the bisulphate as in the normal

sulphate. In the same manner we have the salts sodium carbonate and sodium bicarbonate, etc.

160. Classification of Bases. Bases are classified in a manner similar to the classification of acids, except that it is *based upon the hydroxyl ions instead of the hydrogen ions*. Bases like sodium hydroxide, NaOH , potassium hydroxide, KOH , etc., containing one hydroxyl ion are known as monacid bases; those containing two hydroxyl ions, as calcium hydroxide, Ca(OH)_2 , barium hydroxide, Ba(OH)_2 , etc., are known as diacid bases; while those containing three hydroxyl ions such as ferric hydroxide, Fe(OH)_3 , aluminum hydroxide, Al(OH)_3 , etc., are called triacid bases.

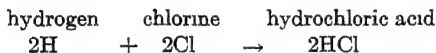
161. Classification of Salts. Since a salt may be regarded as the combination of an acid with a base we may classify the salts in the same manner. Thus if there are neither hydrogen nor hydroxyl ions in combination with the remainder of the salt it will be known as a *normal salt, and these are usually neutral*. On the other hand if only part of the hydrogen of the acid has combined with the hydroxyl of the base there will be a part of the hydrogen left in combination with the salt, making what is called an *acid salt*; or if there is not enough hydrogen to combine with all of the hydroxyl so that part of it enters into the salt it will then be called a *basic salt*. It naturally follows that with a tribasic acid, such as phosphoric, H_3PO_4 , we may have three series of phosphates, such as mono-potassium phosphate, KH_2PO_4 ; di-potassium phosphate, K_2HPO_4 ; and normal or tertiary potassium phosphate, K_3PO_4 . With a triacid base, such as bismuth hydroxide, Bi(OH)_3 we may obtain normal bismuth nitrate, $\text{Bi(NO}_3)_3$, or the basic nitrates, $\text{BiOH(NO}_3)_2$, $\text{Bi(OH)}_2\text{NO}_3$, or BiONO_3 . Theoretically we may obtain as many kinds of salt as the number of ionizable hydrogen atoms in the acid or hydroxyl radicals in the base, but practically many of them are still unknown.

162. Conditions Under Which a Normal Salt May Be Acid or

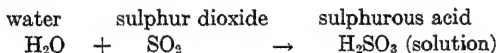
Alkaline. There are certain conditions under which a salt known as a normal salt may be either acid or alkaline. Strong acids are those that ionize readily, such as sulphuric or nitric, and weak acids are those that ionize only to a limited degree, such as carbonic and hydrocyanic. In the same way we have the strong and the weak bases. It follows that *when a strong acid reacts with a weak base the resulting salt is acid in its reaction with litmus*, though normal in its constitution, such as copper sulphate; while *a weak acid reacting with a strong base will give a salt that is alkaline*, such as sodium carbonate, Na_2CO_3 , or potassium cyanide, KCN.

163. Formation of Acids. Three common methods of making acids are—(1) the direct combination of the elements forming the acid; (2) the action of water upon the oxide of a non-metal; (3) the interaction of sulphuric acid with a suitable salt that contains the radical desired in the acid.

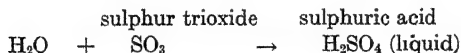
(1) *Direct Combination of Elements.* This method is not commonly used, but may be seen in the formation of such acids as hydrochloric, hydrofluoric or hydrobromic, thus—



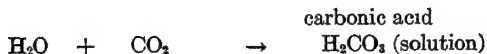
(2) *Action of Water Upon the Oxides of Non-metals.* Oxides of non-metals will combine with water to yield acids, as may be seen when we add a little water to a jar of sulphur dioxide—



With sulphur trioxide we get the equation

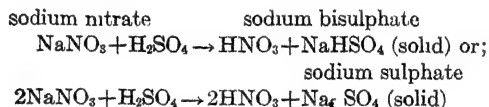


With carbon dioxide the equation is



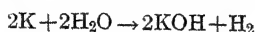
This process is becoming more important with the growth of the use of the contact process for making sulphuric acid, (§298); and the electrolytic process for making nitric acid, (see §725).

(3) *Action of Sulphuric Acid with a Salt.* This is the common method and is the one mostly used in the laboratory. If we take such a salt as sodium nitrate and heat it with sulphuric acid we find that the nitrate acts easily upon the acid, which parts readily with its hydrogen, yielding nitric acid and sodium acid sulphate if the temperature is moderate, or sodium normal sulphate if the temperature is higher and double the amount of the nitrate is used. The same general method applies to the making of hydrochloric acid from the action of sulphuric acid and salt. The equation for the former is



The sulphuric acid is used in a somewhat diluted form and the reaction is in accordance with the ionic theory, where the sodium chloride ionizes and the more active sodium displaces the hydrogen from the acid. The equations for sodium chloride are found in §159.

164. Formation of Bases. (1) *Soluble bases* are usually made by the action of potassium hydroxide, sodium hydroxide or calcium hydroxide upon certain salts of the metal that is to form the base, by uniting with the radical OH. Sodium hydroxide is formed by the action of sodium carbonate and calcium hydroxide. Sodium chloride is not used because the calcium hydroxide will not break it up. Soluble bases may be formed by the reaction of an active metal with water, as



Soluble bases such as NaOH and KOH are now made on a large scale by electrolysis, see Chapter 17.

(2) *Insoluble Bases.* Insoluble bases are made by mixing two solutions, one containing a soluble base, and the other a soluble salt of the metal wanted in the insoluble base. Thus we may make ferric hydroxide, $\text{Fe}(\text{OH})_3$, by mixing a solution of ferric chloride or any other soluble ferric salt, with sodium hydroxide, or any other soluble hydroxide. The term "soluble" is used here as elsewhere in a relative sense, depending upon the degree of solubility.

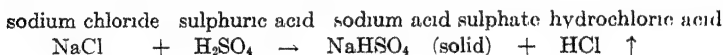
(3) *Bases From Metallic Oxides.* Many of the metallic oxides form bases when water is added, as may be seen when water is added to magnesium oxide, sodium oxide, potassium oxide or calcium oxide. However, not all of the metallic oxides are basic, and we notice that manganese heptoxide, Mn_2O_7 , chromium trioxide, CrO_3 , and some others are in reality acid anhydrides, but as a general rule we may say that the metallic oxides form bases just as the non-metallic oxides form acids when water is added, the exceptions usually coming in the higher oxides of the elements that are both base forming and acid forming.

165. Formation of Soluble Salts. There are several methods of forming soluble salts. The first to be considered is the *neutralization of a base by an acid*. This has already been described in §153. As stated before, we may, for convenience, regard all salts as being formed by this process, although in practice many other methods are followed.

(2) *The Interaction of a Metal and an Acid.* When an acid is added to a metal the two interact about as follows: the metal, if it is more active than hydrogen (see list, §36), displaces the hydrogen from the acid, setting hydrogen free and combining with the acid radical to form a salt. With certain acids such as hydrochloric or sulphuric the hydrogen will be given off without any further reaction, but with others, such as nitric, the hydrogen reacts as a reducing agent with a part of the acid, and is not given off as free hydrogen. Water is formed by the oxidation of the hydrogen, and the nitric radical, which furnishes the oxygen

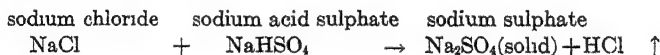
for the oxidation, is reduced to one or more of the oxides of nitrogen (§135) or to other substances depending upon the strength of the acid, the metal used, the temperature, etc. The salt that is formed dissolves in the liquid—chiefly water—from which it may be crystallized by slow evaporation. Some soluble salts can not be made in this way, since the metal will not react with the given acid. Thus, silver and acetic acid or gold and hydrochloric acid will not react, although both silver acetate and gold chloride are soluble. The acids may act upon the oxide of the metal instead of the metal. The hydrogen is oxidized to water under such circumstances.

(3) *By the Action of an Acid Upon Another Salt.* An acid may react with another salt, or with oxides, sulphides, etc., to form salts. Sodium acid sulphate is formed by the action of sulphuric acid upon sodium chloride, thus



A similar reaction occurs when the sulphuric acid reacts with sodium nitrate (§163).

(4) *A Salt May React With Another Salt.* Certain salts may react with other salts to form a third kind of salt. Thus if the sodium acid sulphate formed as above is heated to a higher temperature with more of the sodium chloride, the normal sodium sulphate will be formed together with more of the hydrochloric acid, thus



while if it is added to more of the sodium nitrate the same normal sulphate is formed with nitric acid, thus

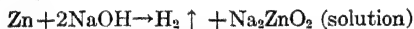


or if we heat sodium bicarbonate the normal carbonate is formed

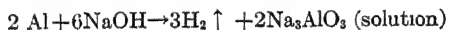


We may notice in connection with this the formation of the so-called *double salts*, such as potassium aluminum sulphate, or common alum, $K_2Al_2(SO_4)_4 \cdot 24H_2O$ and other double sulphates; double chlorides as K_2PtCl_6 ; double cyanides as $KCN \cdot AgCN$, etc. It will be noticed that the *acid radical in the case of double salts is the same for both metals*. Otherwise the more positive metal will unite with the more negative radical, while the less positive metal will unite with the less negative radical, in accordance with the theory of metathesis. (See §27.)

(5) *The Action of a Base on a Metal*. When a metal reacts with an acid it acts as a base forming element, but there are certain metals that will, under the proper conditions, react with a base, thus acting as an acid forming element. If a concentrated solution of sodium hydroxide is added to some zinc and the mixture is boiled, a reaction occurs between the metal and the base, evolving hydrogen and forming the soluble salt known as sodium zincate

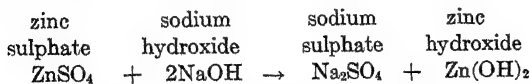


If aluminum is used in place of the zinc the reaction gives sodium aluminate, thus,



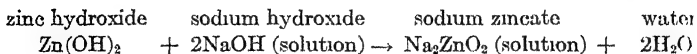
Iron powder might be used in place of the zinc or aluminum and either potassium hydroxide or calcium hydroxide might be used in place of the sodium hydroxide.

(6) *The Action of a Base on a Salt*. Salts are occasionally formed by the action of a base on a salt, as when sodium hydroxide solution is added to a solution of zinc sulphate. The first reaction gives, by metathesis, a white gelatinous precipitate of zinc hydroxide with sodium sulphate:

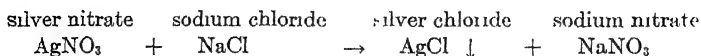


If more of the sodium hydroxide is added to the zinc hydroxide

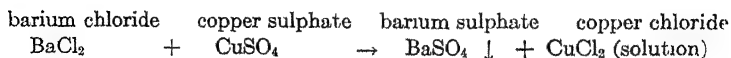
a further reaction occurs and we obtain soluble sodium zincate and water—



166. The Formation of Insoluble Salts. Insoluble salts may be made by mixing two solutions, one containing the required metallic part united to a non-metallic element or radical, while the other contains the required non-metallic part united to a metal. If solutions of silver nitrate and sodium chloride are mixed we obtain an insoluble precipitate of silver chloride in a solution of sodium nitrate—

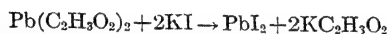


Since the formation of the AgCl depends upon the ionization of the AgNO₃ and NaCl forming Ag and Cl ions, hydrochloric acid or *any other soluble chloride producing Cl ions will give the insoluble silver chloride*, but the second substance will vary with the nature of the soluble chloride. In the same manner we may obtain a precipitate of insoluble barium sulphate when we add a solution of *any soluble sulphate* to a solution of barium chloride—



A study of the table of solubilities, given in Table 6, will readily show the student that practically all of the salts of ammonium, lithium, sodium and potassium are soluble in water; and that nearly all acetates, bromides, chlorates, chlorides, iodides, nitrates and sulphates are soluble in water. The most common exceptions are silver chloride and the sulphates of lead, strontium and barium. With a little practice the student can readily pick out the insoluble salts very accurately by noting the metal and the radical. The salt may contain no indication of solubility as Ag₂CrO₄; it may contain one indication of solubility as Na₂CO₃ or Pb(C₂H₃O₂)₂; or it may contain two

indications of solubility as KCl , NH_4NO_3 , Na_2SO_4 , etc. Naturally, when two salts are formed in a reaction and one forms a precipitate, the precipitate will be the salt showing the fewer indications of solubility. Thus when solutions of lead acetate and potassium iodide are mixed a precipitate of lead iodide is formed



167. Naming of Chemical Compounds. Although there are at this time only 83 recognized elements, the number of compounds is unlimited, since the elements may combine among themselves in many ways. Most of the names of elements were chosen at will and were intended to suggest some prominent characteristic of the substance, and the same was true of the chemical compounds until the enormous number made a more logical naming absolutely necessary, whereby the composition of the compound is told by the name. As stated in §21 every element has a definite symbol which is taken to stand for one or more of three things (1) one atom of the element (2) any indefinite amount; and (3) one gram-molecule. In our study of valence and equations, the *gram molecule* or *mole*, i.e., a number of grams equal to the molecular weight, must be taken as the basis for practical work; but in the naming of chemical compounds we have to consider the symbol rather as standing for an atom and when the symbol is followed by a small figure it means that many atoms of the element. A figure after a radical in parentheses indicates that the radical is taken as many times as the value of the figure. A figure preceding the formula of a compound means that the entire compound is taken that number of times. Thus $5\text{Fe}_2(\text{SO}_4)_3$ would mean that five molecules of ferric sulphate are taken. In each molecule are two atoms of iron, combined with three radicals of SO_4 . In each SO_4 radical are four atoms of oxygen.

168. Metals and Non-metals. It is customary to divide elements into metals and non-metals according to their char-

acteristics. Metals may be described briefly as opaque, conductors of heat and electricity, with a luster that does not disappear under the burnisher, and are often able to displace hydrogen from dilute sulphuric or hydrochloric acid. They are the *base-forming elements*. The non-metals have, for the most part, opposite characteristics and are known as the *acid-forming elements*. The distinction is not a sharp one since *some elements act as both acid-forming and base-forming*. Most compounds are composed of a metallic or electro-positive element or radical combined with a non-metallic or electro-negative element or radical. It is customary to place the more electro-positive part of the compound first, as NaCl, but there are a few exceptions, such as NH_3 , etc.

169. Binary Oxygen Compounds. Binary oxygen compounds contain *one other element* with oxygen. They are known as oxides and are divided into two classes (1) metallic oxides, which usually unite with water to form a base, or hydroxide; and (2) non-metallic oxides, which usually unite with water to form acids. (See §164 part 3.)

170. Degree of Oxidation. Since many of the elements have more than one valence or combining power, there may be two or more oxides of the same element. When this is true the *degree of oxidation is indicated by the ending*, the one having the *larger proportion of the other substance*, and therefore, the *smaller proportion of oxygen*, ending in *ous*, as sulphurous oxide, SO_2 ; while the one having the *smaller proportion of the other substance*, and, therefore, the *larger proportion of oxygen*, ends in *ic* as sulphuric oxide, SO_3 . In the same way we have mercurous oxide, Hg_2O , and mercuric oxide, HgO . It should be observed by the student that *the exact number of atoms of oxygen is not indicated by the endings, ous and ic*, but depends upon the valence of the element combined with the oxygen, so that there is no way for him to tell whether a certain oxide ending in *ic* has one, two or three oxygen atoms, until he has learned more about the valence of the electro-positive portion of the compound. Where

there are several degrees of oxidation as in the case of the nitrogen oxides it is always better to state the degree of oxidation by calling the compounds nitrogen *monoxide*, nitrogen *dioxide*, nitrogen *trioxide*, etc.

171. Naming of Acids. Since acids are often formed by the combination of a non-metallic oxide with water we may note a great similarity in the naming of oxygen compounds and acids. As in the naming of oxides it is customary to call the most highly oxidized acid the *ic* acid, as sulphuric acid, H_2SO_4 , while the less highly oxidized acid is called the *ous* acid, as sulphurous acid, H_2SO_3 . This naturally follows from the naming of the oxides of sulphur, SO_3 , and SO_2 , which give these acids respectively when united with water. However, it sometimes happens that after the acids are thus named *other acids having a higher or lower degree of oxidation are discovered*, so that the names no longer represent what they are supposed to and another adjustment is necessary. Thus if we start with hydrochloric acid we find that there are four possible degrees of oxidation and the acids are known as follows:

Hydrochloric acid	HCl
Hypochlorous acid	HClO
Chlorous acid	HClO_2
Chloric acid	HClO_3
Perchloric acid	HClO_4

Here the prefix *hypo*, in the sense of beneath, or with a lower degree of oxidation, and *per*, in the sense of beyond, or with a higher degree of oxidation, are used in addition to the regular endings.

172. Naming of Bases. The same general rules apply to the naming of bases where there is double valence, and we have ferrous hydroxide, $\text{Fe}(\text{OH})_2$, and ferric hydroxide, $\text{Fe}(\text{OH})_3$. Many of the theoretical bases are still unknown.

173. Naming of Salts. Since a salt may be regarded as the combination of an acid with a base the name of the salt is taken

to show both the acid and the base from which it is derived. The name of the salt will be the metallic part of the base followed by the modified name of the acid radical. Thus when ammonium hydroxide reacts with acetic acid the name of the salt formed will be ammonium acetate. An acid ending in *ic* will give a salt ending in *ate*; an acid ending in *ous* will give a salt ending in *ite*. If the acid has a prefix like *per*, *hypo*, *tetra*, *pyro*, etc., the same prefix will be applied to the salt. The following illustrations will show this:

Name of acid	Name of salt derived from the acid
Sulphuric	Sodium sulphate
Sulphurous	Sodium sulphite
Hypochlorous	Sodium hypochlorite
Perchloric	Potassium perchlorate
Pyrogallic	Potassium pyrogallate

The salts of nitric acid are always known as nitrates, those of sulphuric acid are sulphates, those of phosphoric acid are phosphates, those of acetic acid are acetates, etc. From this it may be seen that the only difference between an acid and a salt is that we have *hydrogen in the acid where we have a metal in the salt*. The radical is always the same in the acid and the corresponding salt, so that the *acids are often called the salts of hydrogen* and the difference between an acid and its corresponding salts must depend upon the difference between the electro-positive ions with which the radical is combined rather than upon the radical itself.

174. Other Binary Compounds. Other non-metallic elements instead of oxygen may combine with the metallic elements or the non-metallic elements may combine to a certain extent among themselves, provided we always bear in mind that electro-positive and electro-negative differ also in degree, making the distinction among the non-metals relative. The names given the binary (two-element) compounds will be the name of the metal followed by the name of the non-metal, modified so as to end in *ide*. This ending is an indication of only two elements.

The older ending was *uret*, and what we now call hydrogen sulphide was formerly called hydrogen sulphuret or sulphuretted hydrogen. Where there are two or more valences the same *ous* and *ic* endings are used as with the oxides and the acids, mercuric chloride, HgCl_2 , having a smaller proportion of the metal and a larger proportion of the non-metal than mercurous chloride, HgCl . Combinations with fluorine give fluorides, as calcium fluoride, CaF_2 ; while bromine gives bromides, as potassium bromide, KBr ; iodine gives iodides, as potassium iodide, KI ; sulphur gives sulphides, as ferrous sulphide, FeS , and carbon gives carbides, such as calcium carbide, CaC_2 , or silicon carbide, SiC .

175. Indicators. Whenever an acid reacts with a base in the proper proportions we form water and a salt. This salt may be soluble or insoluble, and if soluble it is hard to tell just when we have added enough of the acid to the base for complete neutralization. If the salt is insoluble it will be thrown down as a precipitate. According to conditions, when the exact point of neutralization is reached, one of three things may happen—(1) there may be a cessation of precipitation; (2) the precipitate may first begin to appear; (3) there may be a change of color.

In many cases none of these things will happen and in order to tell the exact moment of neutralization we have to resort to different methods to *indicate* that the acid and base are present in just the right amounts. This is usually told by an *indicator*, which is a substance that changes color when the solution changes from acid to basic or vice versa. The indicator is either a weak base or a weak acid which dissociates yielding an ion having a different color than the molecule of the indicator itself. Colorless molecules may yield colored ions, or colored molecules may yield ions of a different color. For example phenolphthalein, a weak acid, undergoes practically no ionization in water or in alcohol, but in contact with alkalies it forms salts that ionize in water and the ion apparently is deep red in

color since the solution assumes a deep magenta color in the presence of a base.

Indicators are generally added to one of the substances, but sometimes it is necessary to add a drop or two of the liquid to a drop of the indicator. The common indicators and their uses are:

(1) Phenolphthalein solution is colorless with acids and magenta red with alkalis. It may be used for most mineral acids, for many organic acids and for most alkalis, but is not so satisfactory with ammonium salts, ammonia, bicarbonates, phosphates or borax. It may be used in alcohol, ether or in mixtures of the two which dissolve many organic acids. The results are rapid, and it is satisfactory with weak bases and weak acids.

(2) Litmus solution is more satisfactory if the purified azolitmin is used. This is the active principle of the litmus, and unless the insoluble material is removed the results are not so satisfactory. Litmus solution is weakly alkaline and yields an anion that is blue. In the presence of an acid it assumes a red color, the depth of color depending upon the strength of the acid. It may be used with most mineral acids, some organic acids, with ammonia, and with alkaline hydroxides when free from carbonates. It is not good for phosphoric and arsenic acids and their salts because the change of color is too gradual, and it is unsatisfactory with weak bases, and with many organic acids.

There are a number of other indicators used for special purposes but they will not be described in detail here. The following brief table will give the general characteristics of the ones commonly used in the laboratory, in the presence of either acids or alkalis:

TABLE OF INDICATORS

Name of Indicator	Color with Acids	Color with Alkalis
Phenolphthalein	colorless	magenta red
Litmus	red	blue
Methyl orange	red	yellow
Rosolic acid	yellow	violet red
Turmeric	yellow	brown
Cochineal	yellowish	violet
Purple cabbage	red	green

Sometimes the use of two indicators gives a more accurate end-point than when one is used alone. For example, if 1 drop of a 0.5% phenolphthalein solution and 3 drops of a 0.04% of a thymolphthalein solution are added to the acid solution which is to be titrated, the end-point is shown by the red color of the phenolphthalein but if too much alkali is added a violet color is obtained due to a combination color of the two indicators, or if 1 drop of a 0.02% of a methyl red solution and 3 drops of a 0.04% thymol blue solution are mixed as an indicator, the end-point is shown by an orange color. One drop of $\frac{N}{10}$ alkali in excess causes the solution to become yellow, and another drop produces a green color thus making it easy to tell when exact neutralization has been accomplished.

176. Problems.

1. If air is 21% oxygen, how many grams of air are required to change 18 grams of carbon to carbon dioxide when the carbon is burned?



2. If one liter of oxygen weighs 1.43 grams, how many grams of potassium chlorate are required to produce 8 liters of oxygen? How many grams of potassium chloride are formed by the reaction? (§35).

3. How much potassium chlorate must be decomposed in order to obtain enough oxygen to fill a 36-liter gasometer?

4. How much zinc and how much sulphuric acid must be used to fill a 36-liter gasometer with hydrogen? (§59).

5. What would be the cost of filling with hydrogen a spherical balloon 2 meters in diameter if the zinc costs 8 cents per pound and the sulphuric acid costs 2 cents per pound?

CHAPTER IX

VALENCE AND EQUATIONS

177. Valence. As stated in §21, *valence means the combining or replacing power* of the element or radical. Hydrogen is taken as the standard and its valence is taken as 1. Elements that have the same valence as hydrogen are said to have a valence equal to that of hydrogen, or 1; those that have double the combining power are given a valence of 2, and so on. Substances having the same valence are called equivalent.

178. Valence and the Ionic Theory. The ion of hydrogen is considered as having one positive charge and may accordingly be written H^+ . In the same way all positive elements may be written with the number of charges corresponding to their combining power, and we have Na, K, Ca, Cu, Cu, Fe, Fe, Hg^{++} , Hg^{+++} , Al, Sn, Sn, etc., among the metals; and Cl, Br, N, N, O, S, S, S, etc., among the non-metallic elements, with NO_3 , $C_2H_3O_2$, OH, SO_4 , CO_3 , PO_4 , etc., among the non-metallic or acid radicals. When electrolytic compounds are made into dilute solution they ionize and the electrical charges on each ion correspond in number and kind to the theory that certain elements have the same combining power as hydrogen while others have two, three, four or more times the combining power. (See Fig. 51.)

179. Valence Must be Satisfied in a Compound. In a saturated compound the *valence of each element must be fully satisfied or the compound is unstable* and there is a tendency for the compound to decompose into simple compounds, often with explosive violence, with or without the addition of oxygen from the air. Even when the valence is apparently satisfied the compound is sometimes held together only very loosely and decom-

poses easily if the temperature is raised, e.g., hydrogen peroxide. The logical formation of compounds is the combination of a given number of positive charges with an equal number of negative charges for stable compounds. While the division into positive and negative is to a certain extent arbitrary, we must recognize the fact that just as in the electric current any point may be taken as positive with reference to the points toward which the current flows, and negative with reference to the

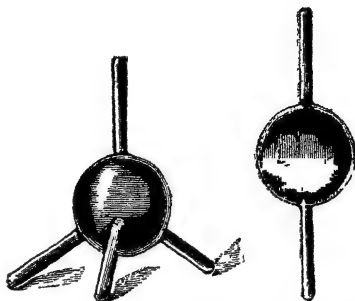


FIG. 51. Carbon and Oxygen Atoms

points from which it flows, so in the list of positive and negative elements we must recognize the fact that *certain elements are more electro-positive than others*, and that while it is not the logical formation we may have a combination of two elements ordinarily classed as negative, since one will be more electro-positive than the other. Thus we may have such unstable combinations as chlorine dioxide, nitrogen triiodide, etc., although the elements composing them are all classed as negative, when compared with those that are strongly electro-positive.

180. Regular Formation of Compounds. Since the number of positive charges must be equal to the number of negative charges in a regular stable compound, we find that a positive element with one charge, or combining power, will unite regularly with a certain amount of a negative element having the same amount of charge. Thus we write HCl , AgBr , KCl , NaCl , etc., or if a radical replaces the non-metallic element we may write HNO_3 , KNO_3 , $\text{NaC}_2\text{H}_3\text{O}_2$, etc. If either of the substances used is bivalent we must use double the amount of the other element, and we would write H_2SO_4 , CuCl_2 , H_2O , etc., or if the positive and negative have the same charge we would

write CuSO_4 , CaCO_3 , etc. If one has a valence of two and the other of three we would naturally take enough of each kind to make the electrical charges equal. Thus in ferrous sulphate we have the formula FeSO_4 , where the iron has a valence of 2, but in ferric sulphate, $\text{Fe}_2(\text{SO}_4)_3$, the iron has a valence of 3. Since in both cases the radical, SO_4 , has a valence of 2 we find that it is easy to tell the number of times each part should be taken by taking each until the total positive charges equal the total negative charges. This gives $\overset{+++}{\text{Fe}} \overset{+++}{\text{Fe}} \overset{=}{\text{SO}_4} \overset{=}{\text{SO}_4} \overset{=}{\text{SO}_4}$ or a total of 6 for either positive or negative and we write the formula $\text{Fe}_2(\text{SO}_4)_3$.

2 016 g. of hydrogen	}	can combine with	{	16. g. of oxygen or 32.06 g. of sulphur
55 84 g. of iron				
40 07 g. of calcium				
46 g. of sodium				
78 2 g. of potassium				
or				
65 37 g. of zinc				
1.008 g. of hydrogen	}	can combine with	{	35 46 g. of chlorine 79 92 g. of bromine or 126 92 g. of iodine
23. g. of sodium				
39 1 g. of potassium				
or				
107.88 g. of silver				
12.005 g. of carbon	}	can combine with	{	4.032 g. of hydrogen 32 g. of oxygen 141.84 g. of chlorine or 319.68 g. of bromine
or				
28 1 g. of silicon				
74.96 g. of arsenic	}	can combine with	{	3 024 g. of hydrogen 106 38 g. of chlorine 239.76 g. of bromine or 380 76 g. of iodine
120.2 g. of antimony				
or				
31.4 g. of phosphorus				
149 92 g. of arsenic	}	can combine with	{	48. g. of oxygen or 96.18 g. of sulphur
or				
240.4 g. of antimony				

The preceding table shows some of the common combinations of elements. The figures show the proportions of each element to be taken.

Of course many other combinations may occur, but these few will show the student some of the proportions existing between the elements of a compound. In the first group, if 2.016 g. of hydrogen can combine with 16 g. of oxygen the formula is H_2O ; in the last group if 149.92 g. of arsenic can combine with 48 g. of oxygen the formula is As_2O_3 . The student should write out all these combinations and any others suggested by the instructor.

The use of valence blocks greatly facilitates the study of valence. These blocks represent the valence of the elements and radicals graphically by the use of different sizes of cardboard upon which the symbols of the elements and formulas of the common radicals are printed. These cards are all the same width, those having a valence of 2 being square, while univalent groups are only half as high, and trivalent groups are three times as high as the univalent. Figure 52 shows some of the uses of the blocks.

181. Valence of Elements. The valence of elements varies from 0 to 8, but the majority of elements have a relatively low valence, and the occurrence of the higher valences is uncommon. It is convenient to divide the elements into those that have a valence of 1, or univalents; those having a valence of 2, or bivalents; those having a valence of 3, or trivalents; those having a valence of 4, or quadrivalents; those having a valence of 5, or pentavalents or quinquivalents; while those having a valence of 6, 7 or 8 are known as sexivalents or hexavalents, septivalents and octavalents respectively.

In writing the formulas of compounds the rules of valence do not always tell us what is the correct formula although they help. When sodium is exposed to the air the combination with oxygen forms sodium oxide, Na_2O , but when sodium is burned the

formula is Na_2O_2 which can be determined only by an accurate analysis. The formula for water is H_2O , and by ordinary valence we would not expect to find H_2O_2 which is the formula

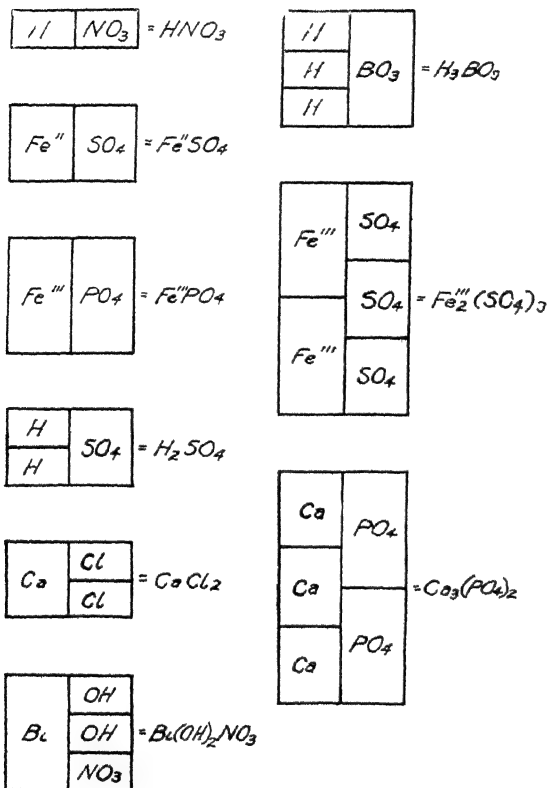


FIG. 52. Valence Blocks.

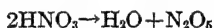
for hydrogen peroxide. The formula for methane is CH_4 which agrees with the valence of carbon and hydrogen. Later we shall see that carbon and hydrogen may combine in many other ways. (See §271.)

182. General Rules for Valence of Elements. The common elements have a *valence of two more often than any other value*, and this is especially true of the metals where the common exceptions are sodium, potassium, silver and lithium which have a valence of 1; platinum, 4; aluminum, 3; bismuth, 3; chromium, 3 or 4; ferric iron, 3; while mercury, copper and tin, and a few others have double valence one of which is 2. Among the non-metallic elements the common gases have a valence of 1 except oxygen, having a valence of 2; and nitrogen, having a valence of 3 or 5. Silicon has a valence of 4; phosphorus, 3 or 5; and sulphur, 2, 4 or 6. There are numerous exceptions to the above valences, since many of the elements have more than one valence, but the ones given are the common valences more often found in the compounds. The valences of the elements other than those that are common are to be found in the table given on the back cover page.

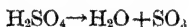
183. Valence of Radicals. In addition to the valence of the elements the student should become familiar with the valence of radicals. This may be divided into two parts—first, the *free valence of the radical as a whole*, and second, *the valence of the distinguishing non-metallic element of the radical*, as sulphur in SO_4 , nitrogen in NO_3 , etc. The first may be determined by the student if he knows the valence of the total metallic part of the compound, thus in H_2SO_4 , the valence of the radical is taken as 2, because it is combined with 2 atoms of hydrogen, each of which has a valence of 1. NO_3 has a valence of 1 because it combines with 1 atom of hydrogen to form nitric acid, HNO_3 , or with 1 atom of any univalent metal to form a metallic salt. The valence of radicals is much more regular than the valence of elements and there are very few exceptions to the valences as given in §155, the only common one being MnO_4 , which has a valence of 1 in the permanganates, and 2 in the manganates. For practice the student should consult the list of chemicals as given in the back of the Manual, where he can pick out the

different compounds and determine the valence from the part he knows.

184. Valence of the Distinguishing Non-metal of the Radical. Every radical acting as a non-metal, that is, a radical that will combine with hydrogen to form an acid, has in it some element besides the oxygen which distinguishes it from other radicals. The valence of this element may be easily determined in this combination by first *deriving the formula for the anhydride of the acid, which will give us a non-metallic oxide*, and from which the valence of the element may be determined by multiplying the number of oxygen atoms by two and dividing that product by the number of the non-metallic atoms. The quotient will give the valence of the element. Thus with nitric acid



The valence of oxygen is 2, making a total valence of 10 for the oxygen in N_2O_5 . There are 2 nitrogen atoms. Ten divided by 2 gives 5, the valence of the nitrogen under the conditions of the combination. In the same way sulphuric acid, H_2SO_4 gives



and the valence of the sulphur is 6. For practice the student should determine the valence of the non-metal in other radicals, whether they occur in acids or salts, using the same method, and applying it to such compounds as HClO , HClO_2 , HClO_3 , HClO_4 , H_3PO_4 , K_2CrO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, MnO_4 , the last, both as univalent and bivalent, etc.

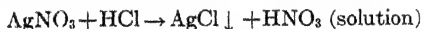
185. Equation Writing. The writing of an equation is in many instances rather difficult, but the great majority of the reactions that occur in elementary chemistry may be expressed by simple equations. The student has observed that in the preceding chapters equations have been used freely, but that very little has been said about the methods of writing them. Certain things must be borne in mind to render the writing of

the simple equations clear and satisfactory. Some of these will be spoken of at this time.

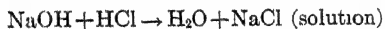
What Kinds of Reactions Occur? We found in §27 that there are four common kinds of reactions in elementary chemistry. These are:

- (1) Analysis, or the breaking up of a compound.
- (2) Synthesis, or the combining of simple elements into more complex substances.
- (3) Substitution, or the replacement of one element or radical by another.
- (4) Metathesis, or the double decomposition and recombination of the parts of two compounds which may be regarded as the mutual substitution of the electro-positive elements.

Of these, metathesis will occur more frequently in elementary work. While it is not always true, yet the student should *look first for metathesis when two solutions are put together, if no gas is given off. There may or may not be a precipitate,* depending upon whether the salt or other substance formed is soluble in the liquid remaining in the test tube.



Here the silver chloride, AgCl, appears as a precipitate, but in

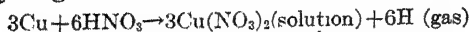


the salt, NaCl, does not appear as a precipitate, because it is soluble in water. Metathesis occurs in neutralizations, in the formation of insoluble salts by precipitation (§166) and sometimes in the formation of soluble salts and soluble bases.

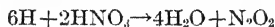
If a metal has been placed in acid and a gas is given off, substitution has occurred. There may be further reaction after the first simple substitution has occurred and just what this is will depend upon the substances used, the temperature, etc.



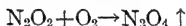
Here the hydrogen is evolved freely as a gas, but in



the hydrogen set free in the nascent condition attacks the nitric acid that is not acted upon by the copper, decomposing it,



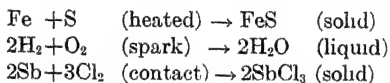
and the nitrogen dioxide at once reacts with the oxygen of the air to form, by synthesis, nitrogen tetroxide, N_2O_4 ,



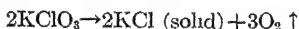
This makes the final equation read



Simple elements heated together if solid, two gases through which a flame or spark is passed, and often solids and the halogens, combine by synthesis to form chemical compounds.



Compounds, when heated either alone or with a reducing agent, frequently decompose into more simple compounds or elements. We have studied potassium chlorate in the preparation of oxygen, and the simple equation is



The ordinary products obtained by heating compounds will be found in §187, part 8.

186. General Suggestions to Aid in Writing Equations.

(1) Study the compound or compounds used. These are known as the *factors* or *doers* because they react. From the table of activity, §36, see if you can find out any thing about any of them. See whether the conditions are best for metathesis, substitution, analysis, or synthesis. Then when the substances are put together and agencies such as heat, flame, etc., are applied, watch carefully what occurs. Is there a precipitate? Is a gas given off? Does the mixture change color? Is heat evolved? Have we used hydrogen, carbon or carbon

monoxide as a reducing agent? What is left? Can we apply the ionic theory of solutions, neutralization or salt formation?

(2) If the student has watched carefully all that has occurred, and has formed a general idea of what he has obtained he should then write down the substances used, and on the opposite side of the arrow place the substances as he thinks he has formed them. Suppose he has neutralized ammonium hydroxide with sulphuric acid. He will first write

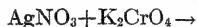


There is a simple method of "balancing" the equation—that is, to see if we have the right formulas throughout, and have satisfied the valence. If the student understands the ionic theory of neutralization he would say, even before attempting to write anything on the right of the arrow, "I have two hydrogen ions; therefore I must have two hydroxyl ions to balance, and thus form two molecules of water." He would at once start his equation again, and because he cannot take the hydroxyl without the ammonium he would take two molecules of the ammonium hydroxide, thus:



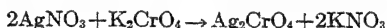
It would be logical for him to write the water first because he should know that in all neutralizations *water is the constant product*, and if he can eliminate that part of the product the part that remains is not complicated. He should then verify the formula $(\text{NH}_4)_2\text{SO}_4$.

In a case of metathesis apply the elimination process. The student mixes some potassium chromate with some silver nitrate and obtains a dark red precipitate. He starts the equation



The silver and the potassium are both positive and both univalent. If there is a chemical change, which he can see from the dark red precipitate, he would say, "Since the silver was combined with the NO_3 before the precipitate was formed it

cannot be combined with it after the change occurs or there would be no chemical change. Since the silver and the potassium are both electro-positive they will not combine together. This eliminates all except the CrO_4 radical which is bivalent and which will, therefore, require two atoms of silver to combine with it." He will then write the equation again



The next question is, "Which is the precipitate? It is either silver chromate or potassium nitrate." In order to determine which one it is he should consult the table of solubility. (See Manual.) He should learn to apply the data on insoluble and soluble salts given in §187 part 1. Since water was used to dissolve the silver nitrate and the potassium chromate originally, there can be no new liquid except what might be formed in the progress of the experiment. None is shown in the equation, and the student would naturally conclude that the liquid in the test tube is water. The table of solubility shows that potassium nitrate is soluble, but that silver chromate is insoluble in water, and he will, therefore, conclude that the precipitate is silver chromate, and not potassium nitrate, which remains dissolved in the water. Thus he obtains a precipitate of silver chromate in a solution of potassium nitrate, in which the chromate is not soluble. The finished equation, therefore, will read



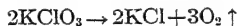
(3) As far as possible the student should study the particular kind of compound used in his experiment, using the index freely, to see if he can find out anything about the way in which the reaction occurs. He can very often find something that will bear directly upon the work he is doing, that will save him much useless effort.

(4) When a substance acts simply as a *catalytic agent* it should not be written in the equation; but if it is written as a factor it must also be written as a product.

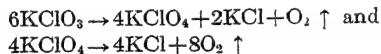
(5) *Water used in solution* is not written as a factor unless it reacts with the other factors. If it is formed as one of the products it must appear with the products on the right.

(6) *Light, heat, electricity* and other agencies are not written as factors of the equation although they are in many cases necessary for the reaction.

(7) *Very few equations express all* that occurs in a reaction. They generally give the average of final results when conditions are approximately the same. Thus in the equation for the reduction of potassium chlorate by heat the student will generally write



However, it is more correct to write it in two parts to show first the formation of the potassium perchlorate, and then the decomposition of the perchlorate into the chloride and oxygen:



By watching the reaction carefully the student will observe that the oxygen always comes off slowly at first, but much more rapidly when the heat is increased near the end of the reaction.

187. The General Behavior of Compounds.

1. *An insoluble precipitate* is formed whenever two solutions are mixed, one of which contains the metallic part, and the other the non-metallic part of an insoluble compound. See the reaction of silver nitrate and potassium chromate, given in §186. The student should remember that *practically all salts of potassium, sodium and ammonium are soluble* and that of the various classes of salts the following are usually soluble: *acetates, bromides, chlorates, chlorides, iodides, nitrates and sulphates*. Thus the student would expect to find potassium sulphocyanate soluble because it is a *potassium* salt. He would expect to find zinc chloride soluble, because it is a *chloride*. He would not expect to find copper carbonate soluble, because

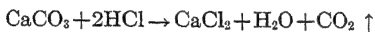
neither *copper* nor *carbonate* is an indication of solubility. He would naturally expect potassium iodide to be more soluble than potassium ferrocyanide since the first compound shows two indications of solubility and the second shows only one. With a moderate amount of practice the student will experience little difficulty in determining solubility. However, some of the most insoluble salts used in elementary chemistry occur as sulphates, iodides, etc., and are exceptions to the regular solubility rules.

2. *If a gas can form it is always liberated.* The gas may (1) escape into the air; (2) dissolve in water if any is present, and the gas is soluble; (3) act upon one of factors bringing about secondary reactions as in the case of copper and nitric acid, §135.

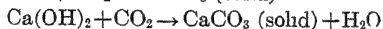
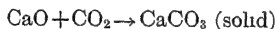
3. *Acids neutralize bases giving a constant product, water (§153). They also react with metals (§165) metallic oxides and carbonates*, if the salt thus formed is soluble, and sometimes act upon a salt, forming another acid and another salt (§165). A reaction of an acid with a metallic oxide is shown in the following equation:



while a reaction with a metallic carbonate is



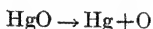
4. *Acid anhydrides* act in about the same manner as acids.



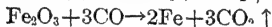
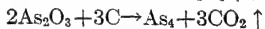
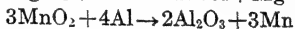
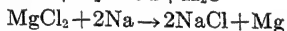
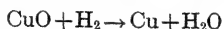
5. *Bases seldom act upon metals*, but strong bases like sodium hydroxide or potassium hydroxide will act upon such metals as zinc or aluminum, where the metal acts as an acid forming element. (See §165, 5.) *Bases will sometimes act upon salts* forming another base and another salt.



6. *Oxides of metals* usually unite with water to form metallic hydroxides. (§164.) Oxides of non-metals unite with water to form acids (§163, 2.) Metallic oxides may be reduced to metals either by heating alone, where the metal is not very active chemically as with mercuric oxide,



or with a reducing agent, such as hydrogen, sodium, aluminum, carbon or carbon monoxide. Illustrations:



7. *Solutions of acids, bases and salts*, reacting with solutions of other acids, bases and salts, generally do not undergo a decomposition of the radical, but the metallic parts exchange places by metathesis.

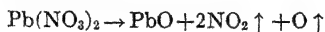
8. *Metallic salts*, when heated, are often decomposed, the products differing according to the salt used, the temperature, etc. Some of the common decompositions are given:

(1) *Carbonates* of the alkaline metals—sodium, potassium ammonium and lithium—cannot be decomposed by heat. Other carbonates can be decomposed either with or without the addition of a special reducing agent. The products are the metal or the metallic oxide, with carbon dioxide or carbon monoxide. Phosphorus and charcoal (carbon) are used as reducing agents.



(2) *Chlorates* are not common, the one used most largely being potassium chlorate. The decomposition gives the chloride and oxygen. (§35.)

(3) *Nitrates* generally give the oxide of the metal, oxygen and an oxide of nitrogen, as



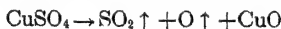
or if the oxide of the metal is easily decomposed, as with mercury, the metal is formed. Sometimes the nitrite is formed with oxygen; or the oxide of the metal, oxygen and nitrogen.

(4) *Nitrites* decompose into oxygen, nitrogen and the oxide of the metal except silver and both nitrites of mercury, which give the metal.

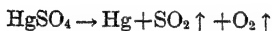
(5) *Oxalates* usually give the oxide, carbon monoxide and carbon dioxide as with lead oxalate; but the oxalates of sodium, potassium, ammonium and lithium give the carbonate and carbon monoxide.



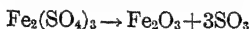
(6) *Sulphates* of sodium, potassium, lithium, ammonium, calcium, barium, strontium, lead and magnesium are not decomposed by heat. However, the sulphates of potassium, calcium and barium may be reduced by heat if mixed with carbon, giving carbon monoxide and a metallic sulphide. Other sulphates require carbon for their reduction and give varying products, such as carbon monoxide, carbon dioxide, sulphur dioxide, a metal or its oxide. Some may be decomposed by heat alone to a metallic oxide, sulphur dioxide and oxygen, as:



but if the metallic oxide is decomposable by heat the residue is the metal, as:



Sulphates of the trivalent metals may be easily reduced, as:



(7) *Sulphites* are usually reduced to form oxides and sulphur dioxide or sulphates and sulphides.

The student is not expected to memorize all of the above rules, but he should at least remember where they are to be found, so that he may refer to them in the writing of equations.

188. Reversible Reactions. When we examine certain reactions we notice that they may proceed *in either direction* and when these conditions are possible the reaction is called reversible. Water may be decomposed into its elements, hydrogen and oxygen, and these two gases may be united again to form water. Water may be partially decomposed by heat, but unless the products are removed as fast as they are formed they will unite again to form water and the decomposition by heat alone cannot be accomplished otherwise.

Mercuric oxide may be partially decomposed by heat, and if exposed to the air the oxygen of the air will unite again with the partially reduced dark red oxide and form the original bright red powder. Not only is this true in these cases but experience shows that under the right conditions, varying with the substances used, *practically all chemical changes can be reversed.*

189. Equilibrium. When a condition is reached where the reaction progresses as fast in one direction as it does in the other a condition known as equilibrium has been reached and *the reaction apparently stops.* If it continues at all it is going in both directions equally, and the conditions are unchanged. For any two substances under the same conditions of temperature, pressure, etc., the proportions required to bring about equilibrium are constant, but these proportions will differ under different conditions.

190. Prevention of Equilibrium. Since in most cases of chemical reaction it is desirable to transform all of our reacting substances, and not merely a part, it is necessary to bring about the reaction in such a manner as to prevent equilibrium. The conditions producing equilibrium may be avoided by *increasing the proportion of one or more of the reagents, or by decreasing the proportion of one or more of the products.* In either case the proportions are changed in such a manner that equilibrium is impossible. This method is known as the effect of *mass action* and the speed of the reaction is increased in one direction only. In practice *the formation and escape of a gas, or the formation*

of a precipitate removes one of the products and permits the reaction to proceed in one direction to completion—such as the action of zinc on sulphuric acid.

191. Fundamental Laws of Combination.

(1) *Law of definite weight.* Any given chemical compound always contains the same elements in the same ratio by weight, if the compound is pure. Thus, by weight, 1 part of hydrogen, 23 of sodium, or 39 of potassium will unite with 19 of fluorine, 35.5 of chlorine, 80 of bromine or 127 of iodine; but double the amount of the metallic element will be required to unite with 16 parts of oxygen or 32 of sulphur. (See §180.)

(2) *Law of Definite Volume.* Any chemical compound made up of gaseous elements always has the same elements in the same volumetric ratio. Thus 1 volume of hydrogen will unite with 1 volume of fluorine, chlorine, bromine or iodine; but 2 volumes of hydrogen are required to unite with 1 volume of oxygen or sulphur vapor; 3 volumes of hydrogen are required for 1 volume of nitrogen, etc. Since all gases have weight the law of definite weight applies to them as well as to other substances.

(3) *Law of Multiple Weights.* When two or more compounds contain the same kind of elements, at least one of the elements has a different weight in each compound, and this is always a simple multiple of its least combining, or atomic weight. Thus we may have iron disulphide, FeS_2 , as well as FeS ; KClO_3 , or KClO_4 ; MnO_2 or Mn_2O_7 .

(4) *Law of Multiple Volume.* In compounds made up of the same gaseous elements at least one of the elements has a different volume in each of the compounds and this volume is a simple multiple of its least combining, (usually atomic) volume. Thus we have water, H_2O , and hydrogen dioxide, H_2O_2 , and others in the same way. Naturally the law of multiple weights applies to all compounds obeying the law of multiple volumes. The compounds of nitrogen and oxygen will illustrate this:

Compound	Formula	Nitrogen by weight	Oxygen by weight	Nitrogen by volume	Oxygen by volume
Nitrogen monoxide	N_2O	28	16	2	1
Nitrogen dioxide	N_2O_2	28	32	2	2
Nitrogen trioxide	N_2O_3	28	48	2	3
Nitrogen tetroxide	N_2O_4	28	64	2	4
Nitrogen pentoxide	N_2O_5	28	80	2	5

192. **Problems.** Complete the following equations

1. $CaO + H_2O \rightarrow$
2. $Ca(OH)_2 + Na_2CO_3 \rightarrow$
3. $Zn + 2HCl \rightarrow$
4. $2NH_4Cl + Ca(OH)_2 \rightarrow$
5. $AgNO_3 + HCl \rightarrow$
6. $NaOH + HCl \rightarrow$
7. $Pb(C_2H_3O_2)_2 + 2KI \rightarrow$
8. $NaNO_3 + H_2SO_4 \rightarrow$
9. $2NaCl + H_2SO_4 \rightarrow$
10. $HgNO_3 + NaCl \rightarrow$

CHAPTER X

ENERGY AND CHEMICAL ACTION

193. The Law of the Conservation of Matter tells us that we can *neither create nor destroy matter* and the *law of the conservation of energy* tells us that we can *neither create nor destroy energy*. We use various forms of energy to bring about chemical action, or we produce one or more of these forms during a chemical reaction, but it is very seldom that an equation tells us anything about the amount of energy we have used or produced.

194. Heat. The reactions involving heat are more numerous than those involving any other form of energy. *In every chemical reaction heat is either liberated or absorbed*, and if two or more reactions are possible the *one involving the greatest heat changes* is the one that *will usually occur*. If the heat is measured it is expressed in calories. The calorie is the amount of heat required to raise the temperature of 1 gram of water 1 degree C., the average of 100 degrees being taken, and this is approximately the same as the amount required to raise the temperature from 15° to 16°. Chemical glassware is usually calibrated for this temperature. The Bunsen burner (Fig. 53) is usually used in the laboratory. It is not as powerful as the Meker burner (see Fig. 54). In the Meker burner the tube is made larger and a nickel grid at the top divides the flame into many small Bunsen flames with the hottest blast of the flame about 2 mm. above the burner. The flame has nearly a uniform temperature throughout, while the Bunsen flame is hottest at the top.

195. Heat Applied to Bring About the Reaction. When heat is required to bring about a reaction it is *sometimes necessary to apply it during the entire process* of the experiment, as when potassium chlorate is decomposed; but there are many others where, after the first application of the heat, the amount

of heat developed by the reaction itself is sufficient to continue the process, as in burning ordinary illuminating gas. If heat is given off in forming a compound it is known as an *exothermic* compound because of this evolution of heat. When a compound is formed with the evolution of heat, it cannot be decomposed by heat alone unless the amount of heat applied is as great as the amount that was given off when the compound was formed. For this reason water is a very stable compound. (See §114.) On the other hand *when heat is absorbed* in the reaction the compound is said to be *endothermic* as in the formation of hydriodic acid, carbon disulphide, ozone, etc. Such compounds are usually unstable when heated.

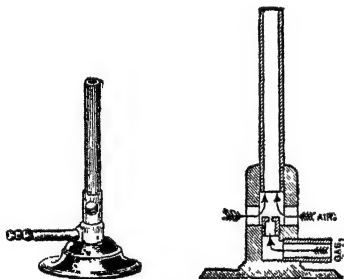


FIG. 53. Bunsen Burner.

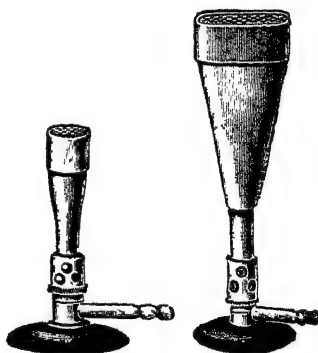
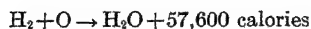


FIG. 54. Meker Burner.

196. The Products of the Combustion of the Common Gases, Liquids and Solids are carbon dioxide, water and occasionally sulphur dioxide. The reactions are all exothermic and the heat equations may be written by adding to the usual equation the number of calories evolved when the substance is burned, or subtracting the number absorbed when the substance is decomposed.



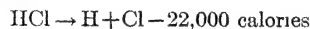
This means that the combined intrinsic energies of 2 grams of hydrogen and 16 grams of oxygen is 57,600 calories more than the intrinsic energy of 18 grams of water.



The term Aq (aqua, water) is taken for any water that is present in which one or more of the substances may dissolve.



When hydrochloric acid is decomposed 22,000 calories are required to bring about the decomposition and the equation would be written



197. Heat of Neutralization. It may be shown by experiment that when gram-molecular weights of the different acids are neutralized by equivalent amounts of the different alkalies *the heat of neutralization is practically the same for all of the different combinations*, being theoretically 13,700 calories, although some combinations vary within the limits of 200 calories, which is not large by comparison. The law holds better for strong acids and bases used in dilute solutions. According to the law of ionization *the molecules of the acid and the base are ionized when in solution*, and if the two solutions are mixed neutralization occurs, *the positive hydrogen ion combining with the negative hydroxyl ion to form the neutral compound, water*, while *the original radical of the acid and the original metal of the alkali form a salt*, usually neutral. Since the acid and the base were both in dilute solution *the salt thus formed will be in dilute solution and will remain partly ionized until the solution is concentrated*. Since the hydrogen and hydroxyl ions always unite, there is no ionization of water, and since the process of neutralization is always the same, the heat of formation must always be the same, namely, that for the combination of one gram equivalent of hydrogen with one gram equivalent of hydroxyl.

Weak acids and weak bases have been defined as those which do not ionize to any extent when made into a dilute solution. *Strong acids and bases* are those that ionize to a large extent when made into dilute solution. When weak acids, such as formic, acetic, phosphoric, etc., are neutralized by strong bases, such as sodium hydroxide or potassium hydroxide, or when strong acids such as nitric, sulphuric or hydrochloric are neutralized by weak bases such as ammonium hydroxide the heat of neutralization varies widely from the theoretical 13,700 calories, even in very dilute solutions.

The weak acids and bases do not dissociate completely and neutralization can proceed only until the dissociated parts have reacted; but as neutralization proceeds more molecules will be dissociated and heat will be either evolved or consumed. This heat will, therefore, either increase or decrease the heat of neutralization, and the heat of neutralization will be equal to the theoretical amount only when the heat of dissociation is equal to zero.

198. Electricity and Chemical Action. Electricity takes part in chemical action in two ways. (1) It may be *produced by chemical action*. (2) It may be used to *bring about chemical action*. Since the modern dynamo has become so widely used, the methods of transforming the alternating current to the direct are so well known, the use of cells of any kind in the laboratory for the production of the electric current is not as satisfactory as more modern methods, although storage batteries and dry cells are used extensively in commerce.

Where the dynamo current is used the student should be familiar with rheostats, methods of cutting down currents, resistance laws, and if the current is alternating, he should know how to change the current to the direct by use of the rectifier (see §206), or by using a rotary converter or motor generator outfit.

Only a brief description of cells will be given in this text, and the student is referred to the various textbooks of physics for descriptions of others not mentioned in this chapter.

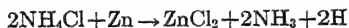
199. Classes of Cells. There are two main classes of cells, *primary* and *secondary*. Primary cells generate their own current from the chemical action between the electrolyte and one of the plates; secondary or "storage" cells must be charged by an external current, which produces a chemical action, changing the nature of the plates in such a manner that after the charging current is removed the electrolyte and one of the plates act in the same manner as a primary cell.

200. Primary Cells are divided into two classes—those for *open circuit* work where the current is wanted for short periods of time, as for ringing door bells; those for *closed circuit* work where a steady current is desired, as in running a motor. Zinc is the metal most often used to react with the electrolyte, and since impure zinc contains small amounts of carbon small local cells may be set up on the surface of the zinc, causing a great waste of material without contributing to the current strength, unless the zinc is amalgamated. *Amalgamation* consists in cleaning the surface of the zinc with acid, and dipping it into mercury, while the surface is rubbed with a cloth. This process brings only pure zinc to the surface and reduces local action to a minimum. Amalgamation may be brought about by the displacement of the mercury from such a salt as mercurous nitrate by dipping the clean zinc into a solution of the salt.

201. Action in a Cell. When zinc alone is placed in dilute sulphuric acid hydrogen is given off and the hydrogen ions unite to form molecules, but when a copper or carbon strip is placed in the solution of acid with the zinc, and the ends are joined with a wire, the ions of hydrogen travel from the zinc to the copper or carbon where they give up their electrical charges before they unite to form the molecule, and in this manner a current of electricity is obtained. The great difficulty is that bubbles of hydrogen have a tendency to cling to the copper or carbon plate after they have given up their charges, and prevent the next ions from giving up their charges, thus diminishing the strength of the current, until it soon falls to zero. This clinging

of the hydrogen to the copper or carbon plate is known as *polarization*, and to prevent it several methods are followed: (1) the plate may be roughened; (2) the plate may be taken out and cleaned frequently; (3) depolarizing substances may be used. A depolarizing substance is usually rich in oxygen so that it reacts with the hydrogen as the latter approaches the plate, and forms water. In this way a steady current may be maintained. The problem of depolarizing, together with that of trying to make a cheap cell having a long life and high electromotive force, has led to the production of a great many different cells, but in this chapter only a few of each type will be described, in order to make clear the fundamental principles.

202. Primary Cells of the Open Circuit Type. (1) In the Leclanché cell a porous cup contains a carbon rod packed in manganese dioxide and pulverized carbon. The filled cup, and a zinc pencil are placed in a glass jar containing a strong solution of ammonium chloride, about 150 grams being used in a jar that will hold a liter. The ammonium chloride is not acted upon by the zinc unless the current is being used, when the equation for the reaction is



The hydrogen passes through the porous cup, where it comes in contact with the manganese dioxide, reacting according to the equation



The latter action is slow and the cell must be given much longer periods of rest than of activity, but with proper care it may be used a year or more before requiring any renewal of parts.

Sometimes the porous cup and the manganese dioxide and pulverized carbon are omitted, the zinc and carbon sticks being placed directly in the solution of ammonium chloride. When this is done polarization is prevented only by allowing the cell

to rest much more than it is used, when the hydrogen passes off into the air slowly.

203. In the Dry Cell the zinc is made into the form of a hollow cylinder with a water tight bottom, and may be lined with absorbent paper. (Fig. 55.) The carbon rod is placed in the zinc cylinder and is packed with zinc chloride, zinc oxide, manganese dioxide, pulverized carbon, and plaster of Paris, made into a paste with water. The top is sealed with bitumen to prevent leaking. The cell is not dry except externally, and as the cell gradually becomes dry internally, the chemical action between the zinc and ammonium chloride becomes less and finally ceases entirely. Fig. 56 shows a vertical section of a dry



FIG. 55. A Dry Cell

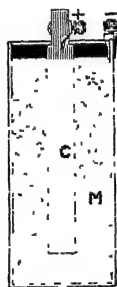


FIG. 56. Vertical Section
of a Dry Cell

cell. The chemical reactions are practically the same as in the Leclanché cell, of which the dry cell is a modification. Owing to the convenience of handling and using, and the small cost of replacing them when worn out, dry cells have practically driven other open circuit cells from the market. The United States now produces annually more than 50,000,000 dry cells and storage batteries valued at more than \$86,000,000.

The deterioration of dry cells kept for any length of time is lessened by coating one of the electrodes with such substances as gelatine, glucose, flour paste or agar-agar.

204. Of the Primary Cells of the Closed Circuit Type, The Daniell Cell is the best known. In a glass jar, containing a strong solution of copper sulphate, is placed a copper cylinder that may be fitted with a perforated pocket for holding crystals of copper sulphate in order to keep up the strength of the solution. (See Fig. 57.) Inside the copper cylinder is placed a porous cup that contains dilute sulphuric acid and a zinc plate that usually has a cross section shaped thus +. The chemical action between the zinc and the acid gives hydrogen and zinc sulphate



The hydrogen passes through the cup where it comes in contact with the copper sulphate solution, with which it reacts according to the equation

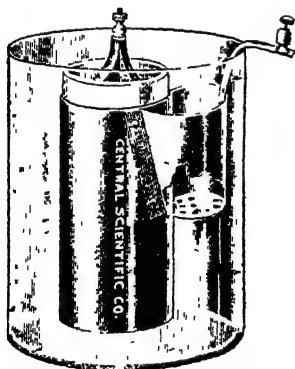
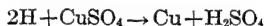


FIG. 57. A Daniell Cell.

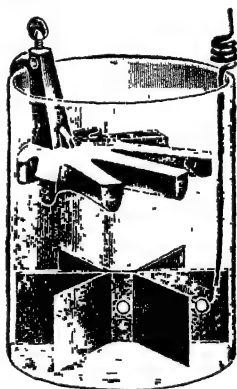


FIG. 58. A Gravity Cell.

The copper, which, like the hydrogen, is electro-positive, travels with the current and is deposited upon the copper cylinder. Since no hydrogen can reach the copper cylinder, polarization is prevented. The sulphuric acid in the porous cup is gradually changed by the action of the zinc into zinc sulphate, and if the

strength of the copper sulphate is not kept up it will in time be entirely reduced to sulphuric acid by the action of the hydrogen.

In the gravity cell the main action is the same as in the Daniell cell. The porous cup is omitted and the liquids are kept apart by gravity. (See Fig. 58). The copper and zinc plates are shaped so as to be held in a horizontal position.

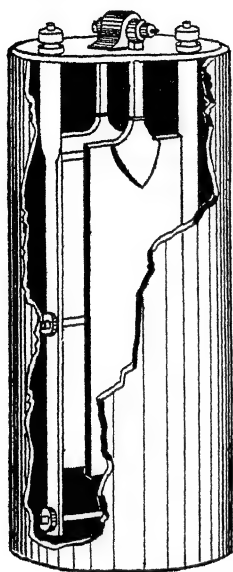
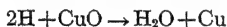


FIG. 59. Edison Primary Cell.

(2) In the Edison primary battery two plates, one of zinc and the other of copper oxide, are both placed in a strong solution of potassium hydroxide, and the whole is covered with heavy oil to keep out the air and to prevent evaporation. (See Fig. 59.) There is no action between the zinc and the potassium hydroxide unless the solution is warmed or unless the circuit is closed. Then the reaction is shown by the equation



The hydrogen passes to the copper oxide plate where it is oxidized to water by the oxygen of the plate, the oxide being reduced to copper.



205. Of the Secondary or Storage Cells the common form is the *lead plate cell*.

In the common form the positive plate has a framework or grid packed with lead dioxide, PbO_2 , and in the same manner the negative plate is packed with spongy (finely divided) lead. (See Fig. 60.) These plates are both placed in dilute sulphuric acid. When the cell is discharging the probable reaction that occurs is represented by the equation

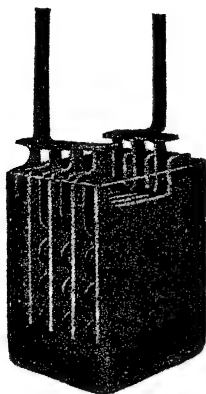
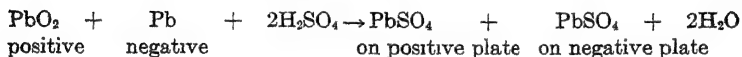
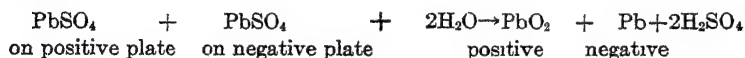


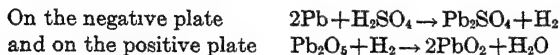
FIG. 60. The Lead Plate Storage Cell.



As the action continues the current gradually diminishes as the plates become more alike. When the cell is charged the equation would read



It is claimed that on charging a cell Pb_2O_5 may be formed instead of PbO_2 , and that lead subsulphate, Pb_2SO_4 is formed in discharging instead of PbSO_4 . The equations for the discharge are given as follows:



The subsulphate of lead is easily oxidized in the air to the white sulphate, PbSO_4 .

A storage cell does not store electricity, but acts as a primary cell after being charged. The charging current must have a higher voltage than the current obtained from the cell, and the time of charging must be more than the time of discharging.

lamp has a tungsten cathode and a carbon anode, and is filled with argon. Each electrode is connected to one terminal of the A. C. line but the current can pass only from the tungsten to the carbon thus giving a pulsating direct current. The small size gives a 2 ampere current of 7.5 volts and the medium size 6 amperes of 15 volts.

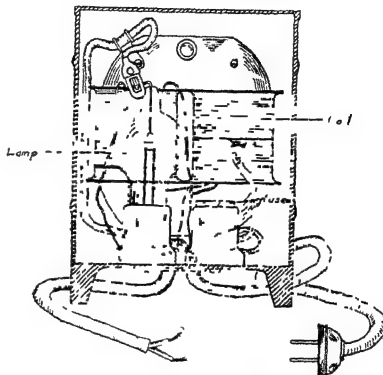


FIG 62 Tungar Rectifier

207. Use of Electricity to Bring About Chemical Action. Electricity is used in two ways to bring about chemical action, (1) to produce intense heat, (2) to dissociate chemical compounds. When the current is used simply to produce heat either the alternating or direct current may be used, the choice depending somewhat upon the construction of the furnace. The simple electric furnace (See Fig. 63) consists essentially of two carbon

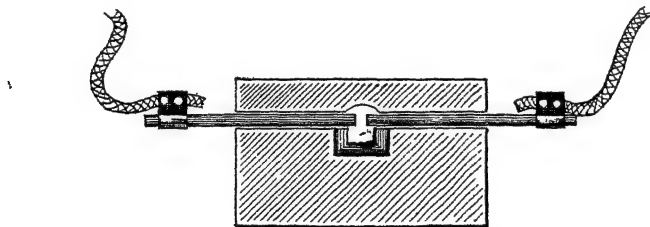


FIG. 63 Simple Electric Furnace.

electrodes placed in a horizontal position instead of in a vertical or right angle position as in the arc lamp. The carbons are surrounded by bricks of lime or other infusible material, hollowed out above and below the electrodes to the depth of a few centimeters. The resistance of the air to the passage of the current

produces the intense heat which is reflected downward from the arched roof of the furnace, giving a temperature varying from 1000° to 3500° depending upon the current and the resistance. In the average electrical furnace of the laboratory only small amounts of material can be fused at a time, but they are often made of large size for industrial work, as at Niagara Falls where the power of the turbines that turn the dynamos is derived from the falling water. This gives special facilities for producing such substances as calcium carbide, CaC_2 ; carborundum, SiC ; artificial graphite, C ; barium hydroxide, $\text{Ba}(\text{OH})_2$; phosphorus, P ; carbon disulphide, CS_2 ; etc., which will be described as they are studied in connection with kindred compounds.

In using electricity for heating purposes the modern laboratory applies it in several other ways—the electrically heated water bath, drying ovens, hot plates, sand bath, flask heater, (Fig. 64), coil heater, crucible heater, water still, muffle furnace (Fig. 65), extraction apparatus, etc., in fact wherever a steady,

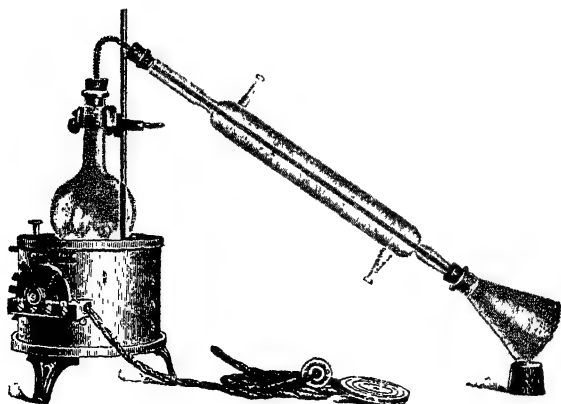


FIG. 64. Electric Flask Heater.

even, easily regulated heat is desired, free from flame, dirt and fumes. In most laboratory apparatus the heat is generated by

the resistance offered by one or more coils of wire to the passage of the current.

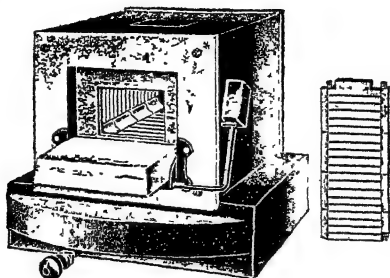


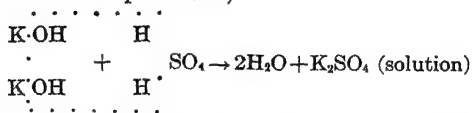
FIG. 65. Electric Muffle Furnace.

208. *The second use of electricity in the chemical laboratory is in the dissociation of chemical compounds, and the applications are many. Electroplating, electrolytic refining of metals, and electrolytic analysis are the main divisions of the applications, but they are all fundamentally the same. The process consists essentially of the following: The terminals of the battery, or the dynamo, are known as positive and negative. These terminals are usually enlarged by attaching to them plates of metal or carbon, and these plates are then dipped into what is known as an electrolytic cell. This cell is usually a dilute solution of an acid, base or salt, and the solution has undergone partial ionization, the molecules separating into the positive ions, or cations, because they go to the negative electrode or cathode; and negative ions, or anions, because they go to the positive electrode or anode. In this, ions obey the law of magnets, that unlike attract, and like repel. The metals, hydrogen and the ammonium radical are the most important cations, and the non-metallic elements and radicals are the anions. (For list of radicals see §155.)*

209. **The Electrolysis of Dilute Sulphuric Acid** is erroneously called the electrolysis of water. When water containing a few drops of sulphuric acid is poured into a suitable vessel, e.g. a Hofmann apparatus, and the current is turned on, bubbles of

gas will be seen to rise in both tubes. The sulphuric acid in dilute solution has been ionized, and when the current passes the positive hydrogen travels with the current and goes to the cathode, while the radical SO_4 travels against the current and goes to the anode. The radical does not collect at the anode, however, but combines with water to form sulphuric acid and to free oxygen. Thus only hydrogen will collect in the tube containing the cathode, and only oxygen will collect in the tube containing the anode, and as these two gases are freed in the right proportions to form water when they recombine the operation is frequently, but incorrectly, called the electrolysis of water. The water disappears because of the chemical action, and not because it is electrolyzed. Pure water does not ionize, and therefore does not conduct the current.

Electrolysis of Potassium Sulphate. If a solution of potassium sulphate is placed in a Hofmann's apparatus and the current is turned on the action at the anode is somewhat similar to that described in the preceding paragraph. The SO_4 , with the accumulation of oxygen, is set free in the same way, but at the cathode the action is more complicated than in the electrolysis of dilute sulphuric acid. Instead of hydrogen, potassium is freed and the metal, instead of collecting on the cathode, decomposes part of the water present and forms potassium hydroxide and at the same time frees hydrogen, as before. We thus have in addition to the two gases, oxygen and hydrogen, an acid and a base in our tubes, so that if the current is reversed we get a further reaction, this time chemical, between the acid and the base, forming water and potassium sulphate, such as we had at the first part of the experiment,



No matter what we take the same general law holds, namely, that the *electro-positive element or radical travels with the current*

to the cathode, and the *electro-negative element or radical travels against the current to the anode*. Secondary reactions of a chemical nature will always occur if any of the products formed by electrolysis can react either with any of the parts of the solutions present or with the electrodes themselves. In many cases platinum electrodes are used, but in the electrolysis of hydrochloric acid or any chloride the ionic chlorine will attack the platinum so that carbon electrodes must be used instead.

210. Electro-plating. In electro-plating the process is essentially the same as just described, differing only in the materials used, while special care must be taken to clean the surface of the article to be plated so that the covering metal will adhere. The cleaned *article is made the cathode* and a *plate of the pure metal desired as a plating is made the anode*. The *electrolyte is a solution of one of the salts of the metal to be deposited as the plating*. It is called the bath. The anode and cathode are dipped into the bath and the current, of *low voltage and relatively heavy amperage*, is turned on. (See Fig. 66.) The solution of the bath, partly ionized,

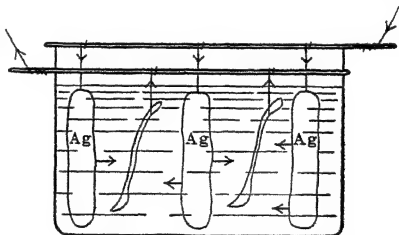


FIG. 66. Electro-plating.

yields the metallic part to travel with the current to the cathode where it is deposited as the plating, while the non-metallic part travels against the current to the anode where it attacks the anode and re-forms the salt used in the bath. In this way the anode is gradually worn away, to keep up the strength of the bath, but the metal deposited upon the cathode comes directly from the solution and will be deposited in the same way until it is all taken from the bath even though a carbon anode is used. The process is the same for all kinds of plating—gold, silver, nickel, copper, etc.—and the differences are essentially in the choice of bath, anode and

rent strength. Some metals do not adhere well to others and when this is the case a preliminary plate of a different metal must first be given. Silver adheres well to copper but not to iron or lead, while copper will adhere to iron or lead, so that if it is desired to silver plate over iron or lead a preliminary plate of copper is given, after which the silver will adhere to the copper.

211. Electrolytic Refining of Metals. This is essentially the same as electro-plating, the chief differences being that the anode is impure and the cathode is made either of the pure metal or of some metal upon which the pure metal may be deposited and from which it may be easily removed. The impurities drop to the bottom of the bath and are removed from time to time.

There is a definite relation between the strength of the electric current and the amount of metal that may be deposited in a given time. This varies practically as the equivalent weight of the metal. A one ampere current will liberate 0.036 gram of hydrogen in one hour, while the same current will liberate 1.18 grams of copper or 4.025 grams of silver.

In stating the proportion between silver and copper, the atomic weight of copper must be divided by 2 for a cupric salt, since the valence of the copper is 2, while the valence of silver is 1. The following proportion has the product of the means very nearly equal to the product of the extremes:

$$31.785 \cdot 107.88 :: 1.18 : 4.025$$

Theoretically the amount of any metal that may be deposited by electrolysis might be used to measure the strength of the current, but practically there are difficulties that appear in many cases. Some metals do not separate uniformly upon the surface of the cathode and do not adhere firmly to it. It is sometimes impossible to wash and weigh the deposit. Some metals are easily oxidized during deposition or when exposed to the air in washing and drying them. Silver yields the most satisfactory results, and copper is considered the next in reliability.

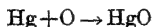
As stated in the discussion of ionization, only certain kinds of solutions conduct the current readily or are decomposed by the current, and in these *the dissociation is greatest in dilute solutions*. Since the *action of ions will be the same no matter what the source*, a study of the ionic action enables the student to tell more easily what to expect in different experiments, where trying to memorize without understanding the fundamental theory would soon become very difficult.

212. Light and Chemical Action. Light may be produced by chemical action or it may bring about chemical reaction. Light is *produced by chemical action whenever the heat produced is sufficient to ignite the gaseous products spontaneously*. Some of these reactions are the ignition of the hydrogen when potassium decomposes water; the flash produced when iodine unites with phosphorus; the spontaneous ignition of phosphorus when rapidly oxidized by the air from a carbon disulphide solution; or when strong sulphuric acid is dropped upon a mixture of powdered potassium chlorate and sugar.

Light brings about a number of chemical reactions, among which are the combination of chlorine and hydrogen in sunlight to form hydrochloric acid; the decomposition of silver salts, which gives the fundamental basis of photography (§478); the decomposition of chlorine water into hydrochloric and hypochlorous acids, and the further decomposition of the latter into hydrochloric acid and oxygen; the decomposition of nitric acid, mercurous chloride and various other compounds, which may be overcome in part by the use of blue or amber colored bottles. These decompositions will be spoken of in greater detail where the compounds are described in the later parts of the text.

213. Problems.

1. How much mercury will be required to combine with the oxygen, freed from acidulated water by a four-ampere current in five hours?



2. How much copper nitrate will be formed by the action of nitric acid

on the copper, freed from a copper sulphate solution by a seven ampere current acting for 10 hours?

3 Write a quantitative equation showing the electrolysis of 10 grams of sodium chloride

4. Write a quantitative equation showing the electrolysis of a mole of potassium sulphate.

THE RELATION OF VOLUME AND MASS OF GASES

The volume of a gas in liters may be found by dividing the number of grams of the gas by the weight of a liter of the gas. The weight of a liter may be found by multiplying the density of the gas compared with hydrogen by the weight of a liter of hydrogen which was given as 0.089873 gram. The density of simple gases is usually the same as their atomic weight compared with hydrogen. Of compound gases it is half their molecular weight. Thus how many liters of oxygen in 17.89675 grams if the density of oxygen is 15.88 compared with hydrogen?

For computations the weight of a liter of hydrogen is taken as 0.089873, and this multiplied by 15.88 gives approximately 1.43 which is contained in 17.89675, or the number of grams, 12.515 times thus giving the number of liters.

It has been found that 22.32 liters of any normal gas weigh a number of grams equal to the molecular weight of the gas.

Thus

22.32 liters of hydrogen weigh 2 grams

22.32 liters of oxygen weigh 32 grams

22.32 liters of carbon dioxide weigh 44 grams, etc

From the above it may be seen that

(1) One gram of any gas occupies a number of liters equal to 22.32 divided by the molecular weight of the gas.

(2) One liter of a gas weighs its molecular weight, expressed as grams, divided by 22.32.

(3) That the volume in liters may be found by multiplying the number of grams of the gas by 22.32 and dividing by the molecular weight. The molecular weight of simple gases may be found in most cases by multiplying the atomic weight by two since they usually contain two atoms per molecule. However, arsenic and phosphorus contain four and mercury vapor has only one atom per molecule.

The weight of a liter of air is 14.475 times the weight of a liter of hydrogen. Since the hydrogen molecule is H_2 , the theoretical molecular weight of air may be taken as 28.95. The relative weight of any gas and air may be found by dividing the molecular weight of the gas by 28.95. Thus SO_2

(molecular weight 64) is easily seen to be approximately 2.2 times as heavy as air: CO_2 approximately 1.5 times as heavy as air, etc

1. How many liters in 10 grams of each of the following gases: Oxygen, hydrogen, carbon dioxide, carbon monoxide, nitrogen, nitrogen monoxide, hydrogen sulphide, ammonia, hydrogen chloride?

2. If you had 10 liters of each of the above gases, what would be the weight of each?

3. Find the relative weight of each of the following gases and air: CO , NH_3 , CH_4 , PH_3 , SbH_3 , C_2H_4 , C_2H_6 , H_2S , N_2 , F_2 , Cl_2 , O_2 .

4. Find approximately the relative weight of each gas in problem 3 to each of the other gases given in the problem. Thus—find the relative weight of CO to NH_3 , then to CH_4 , PH_3 , etc. Work enough to become familiar with the method.

CHAPTER XI

THE HALOGEN GROUP OF ELEMENTS

FLUORINE, CHLORINE, BROMINE AND IODINE

The elements forming this group make one of the best defined groups in the entire list of elements. They are known as the halogens, meaning "to form salt." They are very similar in their general properties and in the compounds that they form, the chief difference being in the activity of their reactions.

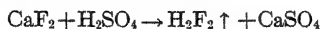
FLUORINE

SYMBOL, F. ATOMIC WEIGHT, 19. VALENCE, 1.

214. Occurrence and Preparation. Fluorine never occurs free, since its great chemical activity causes it to combine with all other common elements except oxygen. It occurs chiefly in combination with calcium, as calcium fluoride, CaF_2 , commonly called fluor spar, or with sodium and aluminum forming a double fluoride, Na_3AlF_6 , called cryolite, which is found largely in Greenland. Free fluorine was first obtained by the electrolysis of hydrofluoric acid, HF, mixed with a little potassium fluoride, KF, contained in a platinum vessel cooled to a temperature of about -50° .

HYDROFLUORIC ACID, HF OR H_2F_2

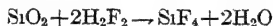
215. Preparation. Hydrofluoric acid is made by pouring a little sulphuric acid upon a paste made of calcium fluoride, CaF_2 , and water. The mixture should be put into a lead or platinum dish because the acid attacks glass readily. The equation showing the reaction is



216. Physical Properties. As used in the laboratory hydrofluoric acid may be either a liquid or a gas, depending upon

the temperature. Above 19.4° the acid is a gas, but below that point it is a liquid if the acid is pure. It becomes solid at -92.3° . The gas fumes in moist air, dissolves readily in water and will always contain water unless special precautions are taken in making it. The aqueous solution distilled at 120° yields a liquid containing about 36.4% of the acid. At 100° the formula is HF, at 30° it is H_2F_2 , and at lower temperatures it is even more complex. The ordinary solution has a specific gravity of about 1.06.

217. Chemical Properties. Pure dry hydrofluoric acid does not act on glass, but when it is moist it forms silicon fluoride, SiF_4 , and the fluoride of potassium, sodium or lead according to the kind of glass. The vapor gives rough depressions, easily visible; but the solution gives smooth, glossy ones. In commercial etching the solution is used. With silica, SiO_2 , the reaction is



After etching the depressions are filled with a paint made by soaking beeswax in gasoline for a week and coloring with lead tetroxide (red); zinc oxide (white), etc.

CHLORINE

SYMBOL, Cl. ATOMIC WEIGHT, 35.46. VALENCE 1.

218. Occurrence. Chlorine occurs in great abundance, but it is always found combined with other elements, such as sodium, potassium and magnesium. Only small amounts occur in nature combined with oxygen or hydrogen. Sea water is about $2\frac{1}{3}$ to $3\frac{1}{3}\%$ solid matter, chiefly sodium chloride, which permits the production of about 5 liters of chlorine from the chlorides found in 1 liter of the water.

219. Preparation. Since chlorine occurs combined it must be prepared by decomposing its compounds. If manganese dioxide and hydrochloric acid are mixed and heated in a flask the hydrogen of the acid is oxidized to water, half of the chlorine

is set free, and the other half combines with the manganese according to the equation



The gas is collected either over salt water or by dry downward displacement (See Fig. 67) since it is soluble in ordinary water and reacts with mercury. Since hydrochloric acid is formed by the action of sulphuric acid on sodium chloride, these two may be substituted for the hydrochloric acid with the final equation



Chlorine is now produced on a commercial scale in large quantities by using the Nelson cell which came into prominence during the World War when 3500 of these were installed at the Edgewood Arsenal, Maryland, with a total production of 100 tons of chlorine per day.

A rectangular steel box contains a perforated U-shaped trough of sheet steel running the entire length of the cell and closed at the ends by cement blocks. This trough acts as a cathode. An automatic feed

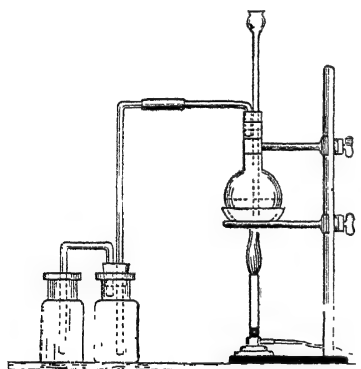


FIG. 67. Preparation of Chlorine.

admits the sodium chloride solution into this trough in which the anodes are suspended. These are specially treated bars of graphite. The perforated cathode is lined with asbestos. The sodium chloride solution is decomposed and chlorine is set free at the anodes while sodium hydroxide is formed at the cathode. The sodium chloride solution passes through the diaphragm and carries with it the sodium hydroxide to

the space outside the cathode. The chlorine goes to the top of the anode chamber from which it is conducted by an outlet pipe and is kept from mixing with the sodium hydroxide solution by means of the diaphragm in the cell. The mixture of sodium hydroxide solution and sodium chlorine solution is separated by evaporating and crystallizing. Under favorable operating conditions the Nelson cell should average $2\frac{1}{2}$ pounds of chlorine and $2\frac{1}{6}$ pounds of sodium hydroxide per hour.

220. Physical Properties. Chlorine is a greenish yellow gas having a disagreeable odor. If chlorine is inhaled in small quantities it acts upon the membranes causing a chlorine cold; if in large quantities death results. At 20° its specific gravity is 2.491 (air = 1) or 35.46 (H = 1). One liter of the gas weighs 3.1674 grams. About 2.2 parts of chlorine are soluble in 1 part of water at ordinary temperatures, and 3 parts at 8° giving chlorine water. Chlorine may be liquefied at 15° with 4 atmospheres pressure or by reducing the temperature a little below -33.6° which is the boiling point of the liquid. Liquid chlorine has a specific gravity of about 1.15, is of a deep yellow color and may be frozen to a greenish yellow solid by cooling to -102° .

221. Chemical Properties. Chlorine is very active when moist, *combining with many substances* readily, but is less active than fluorine and is nearly inactive when dry. In general its chemical reactions may be divided into 3 groups. The first of these groups is the direct combinations of chlorine with elements.

When mixed with hydrogen it remains uncombined in the dark, combines slowly in diffused light, but explodes violently in direct sunlight, or in the light from burning magnesium ribbon, forming a volume of hydrogen chloride equal to the sum of the volumes of the gases taken. Its affinity for hydrogen is so great that it decomposes all hydrogen compounds except hydrochloric and hydrofluoric acids.

With the metals and some non-metals it forms chlorides, many of the substances taking fire when introduced into the gas in a

powdered form. Among these may be mentioned antimony, arsenic, tin, copper, phosphorus, etc. Nascent chlorine from aqua regia dissolves gold and platinum, forming the chlorides of the metals. Melted sodium forms sodium chloride when introduced into the gas.

A second class of reactions includes the *substitution or addition products formed when chlorine reacts with certain compounds*. When dissolved in water the chlorine displaces the hydrogen setting oxygen free, according to the final equation,



With hydrogen sulphide the sulphur is set free,

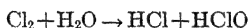


With benzene, C_6H_6 , 1 of the atoms of a chlorine molecule unites with 1 hydrogen atom forming hydrochloric acid while the other atom unites with the C_6H_6 forming $\text{C}_6\text{H}_5\text{Cl}$ and so on until all of the hydrogen has been displaced after 6 molecules of chlorine have been added, so that the final equation would be

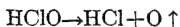


or addition products may be formed the final one with benzene being $\text{C}_6\text{H}_6\text{Cl}_6$.

A third class of reactions are those when *chlorine is used for bleaching purposes*. Dry chlorine does not bleach, but if water is present many substances lose their color. The action is due to the decomposition of the water by the chlorine which gives the equation

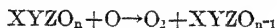


The hypochlorous acid, HClO , decomposes

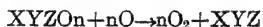


This ionic oxygen reacts with part of the oxygen of the dye, to form a molecule of oxygen. Naturally a color that does not

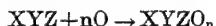
depend upon the presence of oxygen for its permanency, such as printer's ink, cannot be bleached with chlorine. If the formula for any dye containing oxygen is taken as $XYZO_n$ the reaction between the dye and the ionic oxygen may be written



If the reaction occurs n times the final reaction may be expressed by the equation



and the substance is bleached. Any other source of ionic oxygen will do the same work e.g. Na_2O_2 with water is even more rapid than chlorine water. Or if the dye should contain no oxygen and the addition of oxygen bleached it the general equation would be



222. Uses of Chlorine. Chlorine is used for bleaching such substances as cotton, linen, paper pulp, etc., (See Fig. 68) as a disinfectant, where disagreeable gases are present, or for purifying water. It also enters into many compounds, such as the chlorides, chlorates, chloroform, etc.

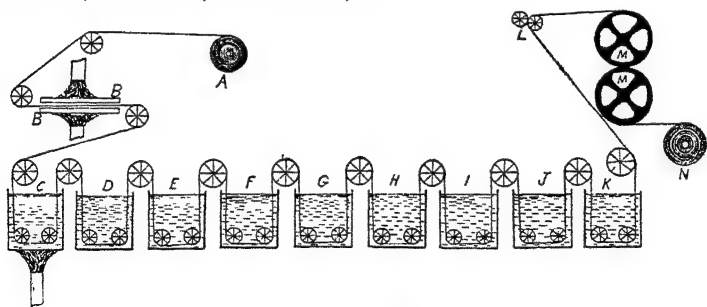
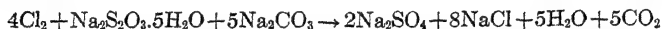


FIG. 68. Commercial Bleaching.

In the European War chlorine has been used to form gas clouds to drive the men from the trenches. Gas respirators are used to enable the men to resist the action of the chlorine. The solution used in one form of gas respirator consisted of

glycerine, 2 oz.; water, 10 oz.; sodium thiosulphate, 15 oz.; sodium carbonate, 5 oz.; with eucalyptus as a refresher. The action of the sodium salts upon the chlorine fixes the chlorine as common salt, NaCl, the equation for the reaction being given as follows:



In addition to the use of chlorine many compounds of chlorine were used in the war. Silicon chloride and titanium chloride were used for smoke screens; chloroacetone, trichloromethyl chloroformate and phenylcarbylamine chloride, benzyl chloride and chloropicrin were used as tear gases; mustard gas is dichlorodiethyl sulphide; sneezing gas is diphenylchloroarsine. It has been computed that more than 50% of the gases used were chlorine compounds, and that approximately 95% used chlorine either directly or indirectly. See Chapter 40.

Some chlorine compounds as carbon tetrachloride, CCl_4 , chloroform, CHCl_3 , dichlorethylene, $\text{C}_2\text{H}_4\text{Cl}_2$, and tetrachlorethylene, C_2Cl_4 , are solvents of fats and greases, and make ideal dry cleaning agents, instead of benzine.

Since 1907 chlorine has been used for the purification of water. The death rate from typhoid decreased from 30.3 per 100,000 in 1907 to 12.3 in 1917. In 2000 tests it was found that from 0.5 to 5 milligrams per liter of water is sufficient to render it safe.

In the purification of water in swimming pools 0.5 pound of chlorine or 1.5 pound of calcium hypochlorite per 100,000 gallons is usually sufficient.

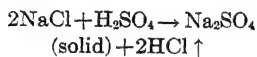
HYDROCHLORIC ACID OR HYDROGEN CHLORIDE, HCl

223. Preparation. Although hydrochloric acid is sometimes found free in nature, as in volcanic gases, it is strictly a manufactured product as it is used. It is one of the products in the manufacture of the sodium sulphates, where common salt is heated with sulphuric acid, either one or two molecules of the

acid being obtained according to the temperature and the amount of salt used. If the reaction occurs at a moderate temperature the following is the equation:



That the reaction is reversible may be seen when a strong solution of the acid sulphate is treated with hydrochloric acid. A precipitate of salt is thrown down. However, if double the amount of salt is used and the temperature is raised the reaction occurs as follows:



The student should compare the reactions of sodium chloride and sulphuric acid with those of sodium nitrate and sulphuric acid. (§133.) It is convenient to call the gas HCl hydrogen chloride to distinguish it from the water solution of the gas, known as hydrochloric acid.

The acid may also be made by the direct combination of hydrogen and chlorine, when the mixture is exposed to strong light, or an electric spark is passed through the mixture. It may be formed by burning a stream of hydrogen in a jar of chlorine, or a stream of chlorine in a jar of hydrogen. A convenient method of generating the gas is to allow concentrated sulphuric acid to drop slowly upon ammonium chloride.

224. Composition of Hydrogen Chloride. Analysis shows that 1 volume of hydrogen unites with 1 volume of chlorine to form 2 volumes of hydrogen chloride. This may be shown by

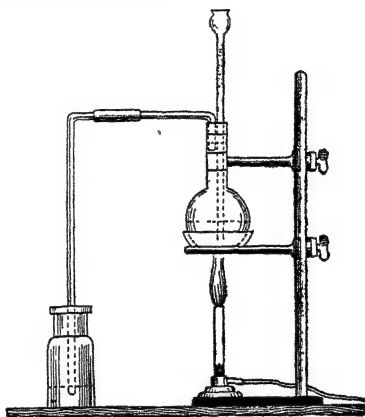


FIG. 69. Preparation of Hydrochloric Acid.

oxygen agent
Electrolytic
Oxygen
hydrogen
iron
sodium
these
rises
another
purified

nt tube with hydrogen chloride gas with a piece of potassium in the bent arm of the tube. When this is metal will unite with the chlorine, and the volume of gas remaining will be found to be exactly half of the volume of gas taken. Hydrochloric acid may be electrolyzed the amount of chlorine will be found to be equal to that of hydrogen, if the gases are not measured until the water has become saturated with chlorine. The electrolysis is carried out with small carbon rods in rubber stoppers, instead of platinum, since ionic chlorine will attack platinum.

Physical Properties. Hydrogen chloride is a colorless, pungent gas, having a sharp taste and smell causing suffocation. One volume of water will dissolve about 500 volumes of hydrogen chloride forming hydrochloric acid and the attraction between the two is so great that white clouds are formed when the gas is exposed to moist air. By cold and pressure the gas is reduced to a liquid that boils at -83.7° and is solid at -114° . At 0° it can be liquefied with a pressure of about 30 atmospheres. The density of the gas is 1.27 (air = 1). A cold solution of the gas has a specific gravity of 1.21 and contains about 42.4% of the dry gas by weight. If a solution of hydrochloric acid is boiled, either water or gas is given off until the solution contains 20.24% by weight of the gas. (Compare the boiling of nitric acid §134.) Its usual color is yellow, due to the presence of impurities such as iron, calcium chloride, and organic matter, etc., and is known as muriatic acid, or so-called chemically pure, "C.P.," acid is the pure gas dissolved in pure water giving a colorless liquid having a specific gravity that varies from 1.19 to 1.20, according to the amount of gas that is dissolved in the water.

229
potassium
with
compounds
It is
yield
Unit
part
23
mixture
a glass
in the
readily

but
chlorine
the
chlorine
chlorine

hydrochloric acid or hydrogen chloride gives a strong acid reaction with indicators. The gas burns nor supports combustion and does not combine with oxygen, although four compounds, varying from HClO_4 , are known. Hydrochloric acid acts upon many

metallic elements forming the chloride of the metal by substitution with the evolution of hydrogen.

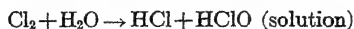
See list of chemical activity, §36, where the metals above hydrogen in the table displace hydrogen from dilute sulphuric and hydrochloric acids.

With the non-metallic elements, such as phosphorus, carbon, sulphur, nitrogen, boron, etc., there is no reaction. With metallic oxides the action is similar to the action with metals, except that water is formed instead of hydrogen. An illustration of the action of hydrochloric acid with metallic oxides may be seen in the preparation of chlorine, (§219).

With hydroxides, hydrochloric acid reacts to form a metallic chloride and water. All metals that decompose water will decompose hydrochloric acid. The acid is monobasic, like nitric acid, forming only one series of chlorides. When heated to 1800° the acid is partly decomposed, but there is a strong tendency on the part of the elements to reunite. Compare the stability of hydrochloric acid with that of water, (§114). For the electrolysis of hydrochloric acid see §224.

227. Uses of Hydrochloric Acid. Hydrochloric acid is used in large amounts as a solvent for metals, to neutralize gas liquor in making ammonium chloride, and as a valuable reagent in the laboratory. Although formed constantly during digestion, 1/8 oz. taken internally may cause death within 24 hours.

228. Hypochlorous Acid, HClO , is a dark yellow liquid that smells like bleaching powder. It is very caustic, destroys the skin, and is a strong bleaching agent. Its salts are hypochlorites. Since hypochlorous acid is very little ionized it is a very weak acid. It is an active oxidizing agent and gives up its oxygen readily. It is formed when chlorine is dissolved in water the equation for the reaction being



The action is reversible. The hypochlorous acid gives up its

oxygen readily and the ionic oxygen acts as the bleaching agent as when moist chlorine is used. (See §221.)

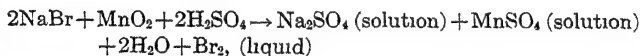
Electrolysis is sometimes used for the purification of sewage. Oxygen and chlorine are liberated at the positive pole to form hypochlorous acid which oxidizes the organic matter and forms iron hypochlorite. At the negative pole potassium oxide, sodium oxide, ammonia, magnesium oxide, etc., are formed and these decompose the iron hypochlorite. Hydrated ferrous oxide rises to the top as a scum mixed with air. It then passes to another tank where the impurities settle and the degree of purification is increased.

BROMINE

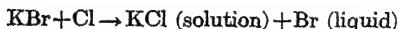
SYMBOL, BR. ATOMIC WEIGHT, 79.92. VALENCE, 1

229. Occurrence. Bromine occurs chiefly as the bromide of potassium, sodium or magnesium and is found in connection with common salt. It never occurs free and is extracted from its compounds that are found in the mother liquors from salt works. It is not very abundant, the bromides in one liter of sea water yielding only 0.01 to 0.1 of a gram of free bromine. In the United States the supply comes chiefly from Michigan, with part coming from Ohio, West Virginia and Pennsylvania.

230. Preparation. Bromine may be prepared by heating a mixture of a bromide, manganese dioxide, and sulphuric acid in a glass retort after the manner of Fig. 45, but with a little water in the receiver. With sodium bromide the final equation will read



but the reaction is more complicated than it appears. Hydrochloric acid is sometimes substituted for sulphuric acid, when the chlorine acts upon the bromide, setting bromine free. Free chlorine may be passed into a solution of a bromide and the chlorine will replace the bromine which is set free, thus:



231. Physical Properties. Bromine is a heavy, dark red liquid, the *only non-metallic element that exists as a liquid at ordinary temperatures*. Exposed to the air it gives off abundant red brown vapors. It boils at about 59° and is solid at -7.3° . Its vapor density is 5.524 (air = 1). The specific gravity of the liquid is about 3.12 (water = 1), making it the heaviest liquid except mercury at ordinary temperatures. It is only slightly soluble, 1 liter of water dissolving 35 grams at 15° . It dissolves in carbon disulphide, chloroform, and ether. Its smell is very disagreeable and it rapidly attacks the membranes, and especially the eyes. On the flesh it produces painful sores. Below 1000° its molecule is Br_2 , but above that temperature it is Br .

232. Chemical Properties. The chemical properties of bromine are very similar to those of chlorine and it acts in the three ways described under chlorine. First it forms bromides with certain metallic elements as aluminum, potassium, sodium, iron, magnesium, etc., and with certain non-metallic elements, as sulphur, phosphorus, etc. It does not combine directly with oxygen, but will unite with hydrogen forming hydrobromic acid, with explosive violence. Second, it forms substitution products with hydrocarbons as benzene, C_6H_6 , in all degrees from $\text{C}_6\text{H}_5\text{Br}$ to C_6Br_6 . Third, it bleaches partly by decomposing the dyes, and partly by freeing oxygen from water so that the dyes are oxidized. When bromine water stands, it decomposes into hydrobromic acid and oxygen, a reaction parallel with that of chlorine water. Bromine water contains about three parts of bromine in 100 parts of water.

233. Uses. Bromine and its compounds are used to the extent of nearly a million pounds annually. It is used in photography, in medicine, chiefly as potassium bromide, sodium bromide and ammonium bromide as a sedative, in the manufacture of coal tar colors and as a disinfectant.

IODINE

SYMBOL, I. ATOMIC WEIGHT, 126.92. VALENCE, 1.

234. Occurrence. Iodine, meaning "a violet color," occurs chiefly with chlorine and bromine, but is found in much smaller quantities than either of the other two. Only a little can be extracted from sea water, but it is absorbed by certain seaweeds and may be obtained from their ashes which contain from 0.5 to 2% of iodine. It also occurs as sodium iodide, NaI, magnesium iodide, MgI_2 , sodium iodate, $NaIO_3$, etc., in the deposits of sodium nitrate in South America, from which it is extracted by means of sulphur dioxide.

235. Preparation. From Seaweed. The weeds are burned at a low temperature and the ashes are exhausted with water which will dissolve out the soluble salts. The liquid is evaporated and the other salts crystallize out, leaving the iodine as potassium iodide in the mother liquor. Chlorine is then passed through the liquor as long as any iodine is liberated, the yield being 1 pound or more from 200 pounds of ashes. (Fig. 70.)

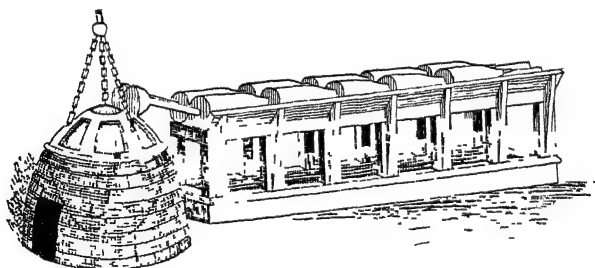
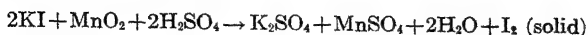


FIG 70 Commercial Preparation of Iodine.

In the laboratory it may be obtained from potassium iodide in the same way that chlorine and bromine are separated from their compounds by the action of manganese dioxide and sulphuric acid. (Fig. 71.)



The iodine passes over as a vapor and may be condensed by cooling, (sublimation). Other iodides may be reduced in a similar way. Either chlorine or bromine will set iodine free from its compounds.

236. Physical Properties.

Iodine is a blue black solid at ordinary temperatures occurring always in a crystallized condition. It has a specific gravity of 4.948 at 17°. It melts at about 115°, and boils at 184°. It is volatile at ordinary temperatures, and the vapor is violet when mixed with air, but intensely blue when pure.

The molecule contains 2 atoms at temperatures as high as 600°. Above 1500° the molecule contains 1 atom. At temperatures between 600° and 1500° both kinds of molecules are thought to exist. This is determined by variations in the molecular weight which decreases as the temperature is raised.

Iodine has a strong taste and a sickening odor. It is only slightly soluble in water, 1 part dissolving in 6000 of water, but it is freely soluble in alcohol, carbon disulphide, ether, benzene, chloroform and a solution of potassium iodide. Its vapor density is 8.716, (air=1) and a liter of the gas weighs 11.32 grams.

237. Chemical Properties. Iodine acts upon the membranes less violently than chlorine or bromine. It colors the skin

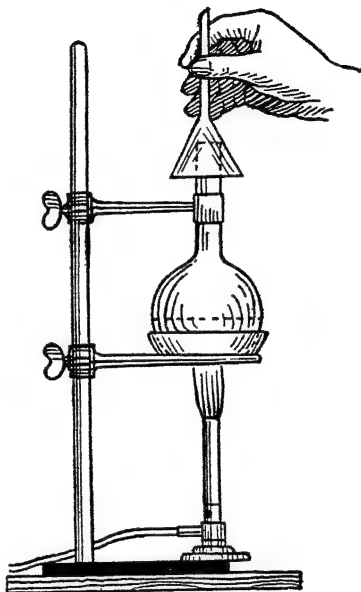


FIG. 71. Preparation of Iodine

yellow-brown, but the color may be removed by potassium iodide solution, or other solvents for iodine. It acts in a manner resembling chlorine and bromine, but less violently. It combines directly with several elements as iron, mercury, phosphorus, sulphur, hydrogen, etc. It is not as good as the other members of the group for bleaching, nor does it form strong substitution products. Phosphorus ignites spontaneously when brought in contact with iodine, forming some phosphorus triiodide and red phosphorus, while abundant vapors of phosphorus pentoxide and iodine are given off. In contact with starch a blue color ranging to almost black appears, and serves as a test both for starch and for iodine. Of all the members of this group iodine has the strongest affinity for oxygen and the weakest for hydrogen. Iodine reacts with silver leaf, brass, copper leaf, aluminum leaf, tin, zinc, cadmium, magnesium and calcium without the application of heat.

238. Uses. Compared with bromine, iodine is used about twice as extensively. It and its compounds find some use in photography, to a certain extent in making aniline dyes from coal tar, and in medicine, where it is used to reduce swellings and in throat affections. Tincture of iodine is made by dissolving (by grinding in a mortar) 7 grams of iodine and 5 grams of potassium iodide with sufficient alcohol to make 100 cc. It is used as a disinfectant in cuts and abrasions. So-called colorless iodine contains no free iodine and does not have the same properties as the tincture. One analysis showed it to be a solution of ammonium iodide, about 4.6%; ammonium sulphite, 2.1%; ammonium hydroxide, 0.95%; sodium iodide, 5%; sodium thiosulphate, 1.6%; sodium sulphate, 15%; in alcohol of 90% strength. Sodium iodide, potassium iodide or ammonium iodide either alone or mixed are probably fully as efficient as this odd combination.

239. Comparison of the Halogen Group.

Occurrence, etc

Element	Source	Exists	Discovered	Uses	Common compounds
Fluorine	CaF ₂	Combined	1886	etching	CaF ₂ , KF
Chlorine	NaCl	Combined	1774	bleach disinfectant as chlorine	NaCl, KCl, MgCl ₂
Bromine	NaBr KBr	Combined	1826	medicine, etc.	bromides of K, Ag, Na, Mg
Iodine	NaI KI	Combined	1811	medicine, etc.	iodides of K, Na, Hg, Pb

Physical Properties

Element	At. Wgt	State	Liquid	Solid	Color	Odor	Vapor density
Fluorine	19	gas	-187°	-223°	greenish	very irritating	1.5
Chlorine	35.46	gas	-34°	-102°	greenish yellow	irritating choking	2.491
Bromine	79.92	liquid	ordinary temperatures	-7.3° at	red brown blue	irritating vile	5.393
Iodine	126.92	solid	to gas	ord. t	black	sickening	8.716

Element	Density of liquid to water	Soluble in vols. of H ₂ O	Weight 1 l. of gas	Boils	Heat of formation	Valence
Fluorine	1.14	decomposes	1.7 g.	-187°	37 cal.	1
Chlorine	1.15	1/3 at 8°	3.1674 g.	-33.6°	22 cal.	1
Bromine	3.12	33	3.547 g.	63°	8.4 cal.	1
Iodine	4.948	6000	11.32 g.	175°-250°	-6.4 cal.	1

Chemical Properties

Element	Bleach	Chem. affinity	Affinity for O	For H	Form insoluble salts with
Fluorine	not used	1	4	explodes in dark	Pb, Hg, Cu, Cd, Fe Zn, Co, Ni, Ba, Sr, Ca, Mg,
Chlorine	good	2	3	explodes in sunlight	Ag, Pb, Hg, Bi, Sb
Bromine	fair	3	2	in flame	same as Cl
Iodine	feeble	4	1	high temp.	Ag, Pb, Hg, Bi, Sb

Element	As a supporter of combustion	Oxygen acids
Fluorine	nearly all metals, hydrogen, compounds, cork, S, Se, Te, P, As, B, Si	none
Chlorine	As, Sb, P, etc.	4
Bromine	Sb, K, etc	3
Iodine	P	2

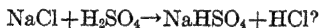
240. Problems.

1. How much hydrofluoric acid may be formed from 10 grams of calcium fluoride by the action of sulphuric acid? (§215)

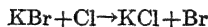
2. How many grams of each of the three products are formed when hydrochloric acid reacts with 50 grams of manganese dioxide?



3. How much sodium chloride and how much sulphuric acid are required to produce 100 grams of hydrochloric acid according to the equation



4. How much chlorine is required to replace all the bromine in five grams of potassium bromide in solution?



5. Write the quantitative equation for the formation of iodine from potassium iodide, manganese dioxide and sulphuric acid.

UNION BY VOLUME

It has been found that when one volume of chlorine unites with one volume of hydrogen, two volumes of hydrogen chloride are formed. In the same way two volumes of hydrogen unite with one volume of oxygen to

form two volumes of steam, and three volumes of hydrogen unite with one of nitrogen to form two of ammonia. This combination is called the two-volume combination, and is very closely connected with the law of the volume and mass of gases giving the same results when worked out in grams

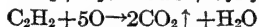
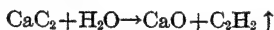
1 How many liters of nitrogen and how many liters of hydrogen will be produced by the complete decomposition of 47 grams of ammonia?

2 How many liters of oxygen in 44 liters of carbon dioxide?

3. How many liters of oxygen and how many of hydrogen in 24 liters of steam?

4. How many liters of chlorine and how many of hydrogen in 18 liters of HCl?

5. How many liters of air (O=21%) are required to burn the acetylene, produced from 10 grams of calcium carbide and how many liters of carbon dioxide are formed?



CHAPTER XII

CARBON AND ITS COMPOUNDS

CARBON, SYMBOL, C. ATOMIC WEIGHT, 12.005. VALENCE 4.

241. Introduction. The number of carbon compounds is so great that adequate treatment of the subject demands several separate volumes, but there are a few compounds that should be studied by the beginner. Some of these will be described in this chapter and the others in several of the later chapters. No systematic treatment of the carbon compounds will be attempted since that belongs to advanced work. More than 200,000 carbon compounds are known and more are being discovered every year.

242. Occurrence of Carbon. Carbon occurs both free and combined. All animal and vegetable substances are rich in carbon, such as starch, sugar, oils, fats, protein, etc. It also occurs in enormous quantities in the carbonates, of which calcium carbonate, CaCO_3 , found in limestone, chalk and marble is the most abundant. It is given off as carbon dioxide during the process of breathing, and is formed when carbonaceous matter is burned in a plentiful supply of air, while carbon monoxide is formed if the air supply is limited. Pure carbon is found in the crystallized state as the diamond, and some graphite; or as amorphous carbon, including all other varieties and much of the graphite.

243. The Diamond is found chiefly in South Africa, India, Borneo, and Brazil and occasionally in the United States. It occurs in the crystalline form, often with curved surfaces and occurs as octahedra and as polyhedra of 24 or 48 faces. (Fig. 72.) It must be cut and polished before it gives evidence of its brilliancy. (Fig. 73.)

244. Physical Properties. Diamond is the hardest substance known, and refracts light strongly when properly cut. The index of refraction is 2.5, while the index for flint glass is 1.6, for crown glass is 1.5, for water 1.33. It is insoluble in all

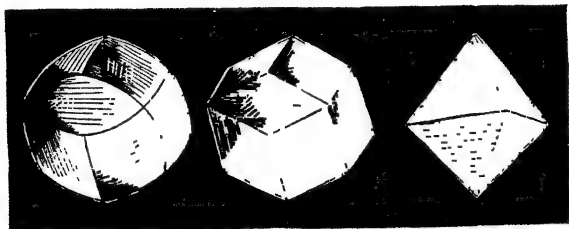
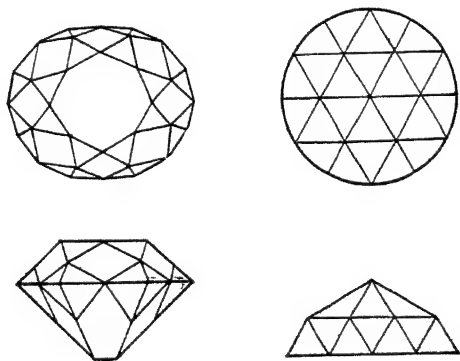


FIG. 72. Diamonds.



BRILLIANT - CUT

ROSE - CUT

FIG 73. Cut Diamonds.

known liquids at ordinary temperatures, but is soluble in molten cast iron. Its specific gravity is 3.51 to 3.55. The colorless varieties are the most highly prized, but it occurs also in blue, green, yellow, brown or black, the latter being used to polish

other diamonds, since they must be polished in their own dust, or they are used for drill points. (Fig. 74.)

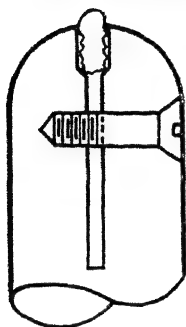


Fig. 74. Diamond Mounted for Cutting.

245. Chemical Properties. When heated without air the diamond swells and turns black, without loss of weight, resembling coke. Heated with air to 700° , it forms carbon dioxide, the amount of the gas being the same as it would be if any other kind of carbon of the same mass were burned. Artificial diamonds of microscopic size have been made by melting carbon in cast iron in an electric furnace heated to about 3000° and plunging the mass into water which chills the outside causing it to contract. This exerts enormous pressure upon the interior of the mass and small diamonds crystallize out. (Fig. 75.) Most of the product

is graphite. In another process pulverized carbon is heated in hydrogen on a spiral of iron wire in the electric arc under a pressure of 3100 atmospheres.



Fig. 75. Artificial Diamonds.

The legal carat in the United States weighs 200 milligrams. The weight before 1913 was 205 milligrams.

246. Graphite, known also as plumbago or black lead, occurs in large quantities in Siberia, Ceylon, Brazil, etc. It is

often crystalline but is usually amorphous. It is produced artificially in making artificial diamonds and is made in large quantities at Niagara Falls as a commercial product. Acheson's process passes a heavy current for several hours through a mixture of 3 to $3\frac{1}{2}$ tons of coke, pitch and a little sand or ferric oxide.

247. Properties. Graphite is a gray black or steel gray solid, having a metallic luster and feeling soft to the touch. It leaves a black mark when drawn over paper and is used for making "lead" pencils consisting of a mixture of graphite and clay. It is insoluble in all liquids, is a good conductor of the electric current and has a specific gravity of 2.3 to 2.7. Heated without air, graphite does not change. Heated in abundant air, it burns to carbon dioxide. Graphite contains a small percentage of impurities since about 0.4% of ash is obtained when it is burned.

248. Uses. Graphite is used for making pencils, crucibles, stove polish, as a lubricant when mixed with such a substance as vaseline, etc. It is also used for electrodes in many electrolytic operations, particularly where chlorine is evolved. See extraction of aluminum, §440, and production of sodium hydroxide, §374.

AMORPHOUS CARBON

249. Charcoal. Charcoal consists of charred wood, bones, blood, etc. It is formed from wood when the wood is burned without excess of air. The wood was formerly piled in heaps, covered with earth and lighted. After burning for a considerable time the fires were extinguished, and the wood was found to be charcoal. (Fig. 76.) Various gases and liquids given off in the process were allowed to go to waste. This included wood (methyl) alcohol, acetic acid, acetone, etc., which were not considered worth saving. Now there are large plants for the manufacture of methyl alcohol and acetic acid, and the charcoal, once considered the principal product, is called a by-product. The

distillation is carried on in special retorts so arranged that all the gases and liquids are saved. In either method the charcoal is not burned, because there is no oxygen present with which it can combine. The charcoal will weigh about 15 to 25% of the original weight of the wood, but it retains the same shape. Charcoal is an impure carbon and always contains some incombustible substances that are found in the ashes when it is burned.

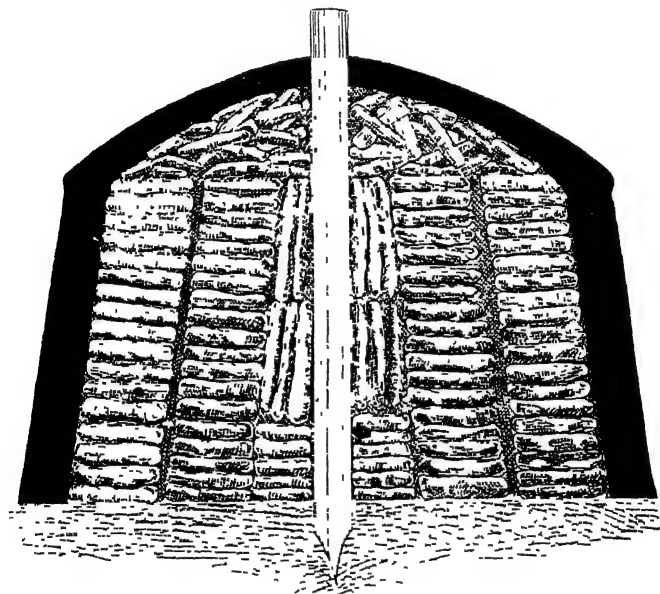


FIG. 76. Old Method of Making Charcoal.

250. Physical Properties. Charcoal is a black, lustrous, rather soft solid. It is insoluble in liquids, but dissolves in molten iron, forming graphite. It absorbs gases from the air or from water, the amount depending both upon the nature of the absorbed gas and upon the porosity of the charcoal used, some varieties absorbing twice as much gas as others. Hence its

use in filters. Its specific gravity is not over 1.57, which causes it to sink in water if powdered, but its porosity causes it to float when it is not powdered.

251. Chemical Properties. Heated without air charcoal does not change. Heated in air, it forms carbon dioxide or carbon monoxide, according to the amount of oxygen present. It does not decay as rapidly as wood, because there is less variety of materials to decay. Hence fence posts, piles, etc., are often charred, which causes them to last for many years.

252. Bone Black or Animal Charcoal is formed from charred bones. It is very fine, since the animal matter is only about one-third of the bone, and is distributed throughout the bony material. The rest of the bone is chiefly calcium phosphate. Bone charcoal must be purified by hydrochloric acid and by washing with water. Like wood charcoal, it is porous and will absorb gases and remove odors from liquids. It is used in the whitening of sugar, since it destroys many vegetable colors. Bone black as made usually contains about 90% of calcium phosphate.

253. Lamp Black or Soot is formed when a cold object is depressed in the flame of burning oil, tallow, resins, etc., or when the supply of air is partially cut off, otherwise the substance burns to carbon dioxide and water. It consists of fine carbon mixed with some of the unchanged oil. It is used in printer's ink and cannot be easily destroyed.

254. Coke is formed when coal is distilled without air. It has the same relation to coal that charcoal has to wood. Part of the product when coal is distilled is a very hard carbon known as gas carbon, which conducts electricity like a metal, and is used in batteries and as carbon pencils in arc lamps.

255. Coal. There are many varieties of coal, the best known varieties in the United States being the anthracite, or hard coal, and the bituminous, or soft coal. Lignite and peat are not true coals but resemble coal in many ways and are used extensively as fuels. (See Chapter 33.) They are all formed from the decay

of vegetable matter under pressure, with a limited supply of air. Peat is formed in the earliest stages, while lignite is more closely allied to wood. It has more varieties of impurities than bituminous coal. Bituminous coal is a brilliant black variety, containing 75 to 88% of carbon and the rest is earthy or bituminous matter. It is particularly rich in gases and volatile liquids, and is used for making illuminating gas by the older process, giving as by-products, coke, coal tar, ammonia, etc. (Fig. 77.)

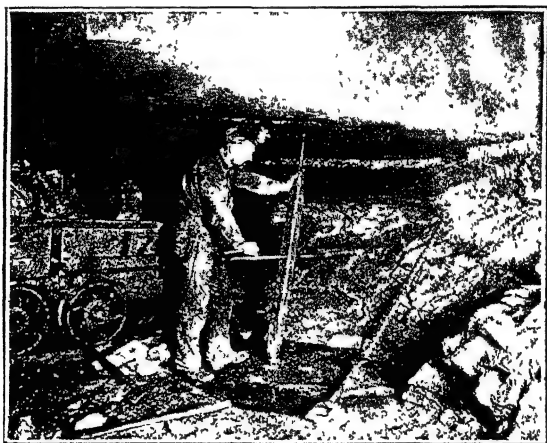


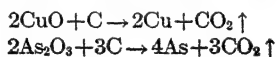
FIG. 77. Coal Mining.

Anthracite, or hard coal, contains 90 to 92% of carbon and the rest is earthy matter. It is more compact than the other varieties and requires greater pressure for its formation.

256. Allotropism. These various forms of carbon illustrate allotropism which has been spoken of under oxygen and will be met with in a few other cases, as in the study of sulphur, phosphorus, etc.

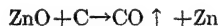
257. General Properties of Carbon. All forms of carbon have the same general physical and chemical properties. All

forms burn to carbon dioxide if enough oxygen is present during the combustion; otherwise carbon monoxide is formed. At the high temperature of the electric furnace, carbon combines with calcium, forming calcium carbide, CaC_2 , with silicon, forming silicon carbide, SiC , called carborundum. Under proper conditions it combines with hydrogen, sulphur, etc. Carbon is used extensively as a reducing agent, and will reduce every known oxide if the temperature is sufficiently high.

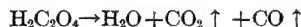


CARBON MONOXIDE, CO

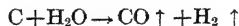
258. Preparation. Carbon monoxide may be prepared in several ways. The reduction of zinc oxide with carbon will give it thus:



It is formed when oxalic acid is heated with several times its weight of sulphuric acid. The oxalic acid breaks up thus:



The water is absorbed by the sulphuric acid. The carbon dioxide may be removed by passing the mixed gases through a solution of sodium or potassium hydroxide and the carbon monoxide is collected over water. It is formed when carbon dioxide is passed over incandescent carbon and thus is always formed at the central part of a coal fire. At the bottom of the grate the carbon burns to carbon dioxide; as this passes upward it combines with more carbon and burns at the top of the grate as carbon monoxide, forming carbon dioxide as the final product. Carbon monoxide is formed when steam is passed over incandescent carbon,



the resulting mixture of the monoxide and hydrogen being the chief ingredients of water gas. (See Chapter 33.)

259. Physical Properties. Carbon monoxide is a colorless, odorless, tasteless gas, almost insoluble in water, of which 100 volumes dissolve only 2 volumes of the gas. It is soluble in a solution of cuprous chloride in hydrochloric acid. It is slightly lighter than air. At a low temperature and with great pressure the gas may be condensed to a liquid that boils at -190° and becomes a white solid at -199° .

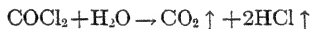
260. Chemical Properties. Carbon monoxide is neutral to indicators and has no effect on lime water, which distinguishes it from carbon dioxide. It burns with a pale blue flame to carbon dioxide, but does not support combustion. It is very poisonous, as little as 0.1% causing death by changing the red corpuscles of the blood, forming a stable compound and preventing the absorption of oxygen. The combustion of gasoline in a gasoline engine produces carbon monoxide and in a closed garage the air near the exhaust becomes dangerous in 10 to 15 minutes and in the farthest parts of the room in 20 to 30 minutes. The collapse usually comes without warning and is almost invariably fatal unless aid comes very quickly since more carbon monoxide will be formed as long as the engine runs. The exhaust from a gasoline engine should never be discharged into a closed room.

Carbon monoxide in the air may be detected by palladium chloride test paper. A 10% solution of palladium chloride is used to moisten filter paper which is then dried in the dark. The end of the strip is then moistened and exposed to the air. If carbon monoxide is present the moistened portion becomes gray, brown, or black in 5 or 6 minutes. One part in 3,000 gives a gray color. If hydrogen sulphide is present at the same time the air should be passed through a solution of lead acetate before entering the vessel containing the palladium chloride.

Experiments carried out for solving the general problem of ventilating in the New York—New Jersey Vehicle Tunnel to determine first, the amount and composition of exhaust gases

from motor vehicles, second, to determine the dilution necessary to render these gases harmless; and third, the rate of air flow, etc., show that 4 parts of carbon monoxide in 10,000 has been found to be the danger limit.

Two volumes of carbon monoxide mixed with 1 volume of oxygen unite to form 2 volumes of carbon dioxide. It is decomposed at high temperatures to carbon and oxygen. In the sunlight it unites with an equal volume of chlorine, forming carbonyl chloride, COCl_2 , a liquid that combines with water, forming carbon dioxide and hydrochloric acid.



With both chlorine and oxygen, carbon monoxide acts as a bivalent radical and is known as carbonyl. It combines with certain metals, as with nickel, forming nickel carbonyl, $\text{Ni}(\text{CO})_4$.

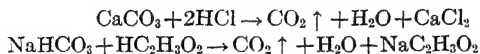
CARBON DIOXIDE, CO_2

261. Occurrence. Carbon dioxide has been known as "fixed air," "chalk acid," etc., and is now popularly called "carbonic acid," or "carbonic acid gas." It occurs in the atmosphere to the extent of about 3 or 4 parts in 10,000. It is given off by the lungs in breathing, is a product of putrefaction, fermentation and combustion; occurs free in the gases of volcanoes, and combined with calcium oxide as calcium carbonate, CaCO_3 , as limestone, marble, chalk, etc. Under the influence of sunlight, the chlorophyll of plants decomposes carbon dioxide, absorbing the carbon and setting the oxygen free, thus overcoming any tendency to large accumulations in any locality. It exists in certain caves, and collects in the galleries of mines when "fire damp," or methane, CH_4 , explodes.



262. Preparation. Carbon dioxide is usually prepared in the laboratory by the action of hydrochloric acid on pieces of

marble, CaCO_3 , or other carbonates, and is collected by dry downward displacement.



It may be formed by burning carbon monoxide, or carbon, in air, but is diluted with nitrogen.

As shown in §261, it is produced by the burning of methane, and, by the miners, is called "choke-damp," or "black-damp." Either $\text{CO} + \text{O}$ or $\text{C} + \text{O}_2$ will give carbon dioxide, the volume of the gas being equal to the amount of oxygen used, showing that the formula of the gas is CO_2 .

263. Physical Properties. Carbon dioxide is a colorless gas with a feeble odor. Its specific gravity is 1.529 (air = 1). One liter of the gas weighs 1.977 grams. It may be liquefied at 0° with 36 atmospheres pressure, or at 20° and 60 atmospheres pressure, forming a colorless liquid that boils at -78° . In a liquid condition it is sold in strong steel cylinders.

Liquid Carbon Dioxide was first introduced in 1885 by a New York firm. Liquefied carbon dioxide is usually sold in steel cylinders, 4 feet long, having an outside diameter of $5\frac{1}{2}$ inches, and weighing when empty 50 to 65 pounds. The bursting pressure of the cylinders varies from 4900 to 5900 pounds per square inch. They are tested to 3700 pounds before filling. The pressure, even at 130°F . is only 2240 pounds per square inch, so that there is little danger from bursting. These cylinders hold 20 pounds of the liquid. A larger cylinder is sometimes used, 51 inches long and $8\frac{1}{2}$ inches in diameter, and holds 60 pounds of liquid carbon dioxide.

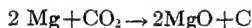
When the cylinder is inclined so that the liquid may run out and the escaping liquid is allowed to flow into a heavy cloth bag the liquid vaporizes so rapidly that part of the liquid is solidified because the heat in the liquid is used to turn more of the liquid to the gaseous condition. If the solid is mixed with ether, a

temperature of about -80° is produced, which is sufficiently low to enable one to perform many interesting experiments.

One volume of water dissolves 1 volume of carbon dioxide under normal pressure at 15° , and the amount of the gas that may be dissolved varies directly with the pressure. When the pressure is removed the gas bubbles through the water and is the cause of the froth on such effervescing drinks as soda water, ginger ale, root beer, etc.

264. Chemical Properties. Carbon dioxide does not burn because it cannot combine with any more oxygen. It does not support ordinary combustion and will support combustion only when the temperature of the burning body is high enough to decompose the gas into free carbon and oxygen. It is a very stable gas, only $7\frac{1}{2}\%$ being dissociated at 2000° .

Such substances as burning potassium, sodium, or magnesium will burn in carbon dioxide,



but most substances are extinguished, 15% of carbon dioxide in the atmosphere being sufficient to extinguish a burning candle, while slightly more suffocates a person. Carbon dioxide is used as a fire extinguisher the gas being furnished by the action of sulphuric acid upon a solution of sodium bicarbonate, the substances being mixed when the container is inverted. (Fig. 78. See also §262.)

If calcium hydroxide, $\text{Ca}(\text{OH})_2$, is mixed with water part of the solid dissolves forming lime water. If carbon dioxide is run into lime water, a white precipitate of calcium carbonate, CaCO_3 , appears in the liquid. A similar result is seen when baryta water (barium hy-

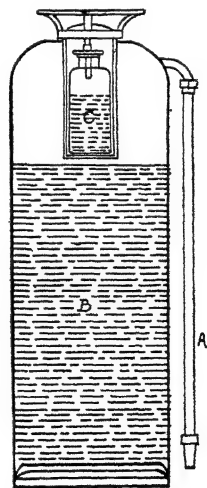
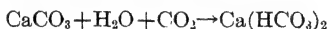


FIG 78. A Chemical Fire Extinguisher.

dioxide, $\text{Ba}(\text{OH})_2$, in water) is used. This serves, therefore, as a test for carbon dioxide and hence, carbonates if the gas is formed by the action of an acid on what is taken to be a carbonate. Water charged with carbon dioxide will dissolve the otherwise insoluble calcium carbonate, since it changes it to the soluble acid carbonate, $\text{Ca}(\text{HCO}_3)_2$



If the gas is driven off by heat or by other methods, insoluble calcium carbonate is precipitated. Thus temporarily hard water may be softened by boiling. A further illustration is seen when water charged with carbon dioxide flows over limestone. The rock is dissolved and if the water has access to a cave the gas escapes and the calcium carbonate is deposited, either as stalactites from the roof, or as stalagmites from the floor. Carbon dioxide is more soluble in alcohol than it is in water. It is not easily reduced by heat alone nor by hydrogen, but may be reduced by carbon to carbon monoxide. It does not support respiration, but is not poisonous.

The action of baking powder depends upon the formation of carbon dioxide, since the substances composing the powder, as potassium acid tartrate (cream of tartar) and sodium acid carbonate (baking soda), produce carbon dioxide when mixed and moistened. (See §373.)

265. Carbonic Acid, H_2CO_3 , is not known except in solution, and is formed when carbon dioxide is dissolved in water. It is very little ionized and therefore exhibits only feeble acid properties. It is a dibasic acid, and its salts are both normal, as sodium carbonate, Na_2CO_3 , and acid as sodium bicarbonate, NaHCO_3 , also called sodium acid carbonate. Both of these salts have an alkaline reaction because they are formed by the action of a strong base, NaOH , with the weak carbonic acid. Many other carbonates are known.

CARBON DISULPHIDE, CS_2

266. Preparation. Carbon disulphide may be prepared by passing sulphur vapor over incandescent carbon; or charcoal and sulphur are heated in cast iron vessels and the distillate is collected in a cooled receiver. (See Fig. 79.)

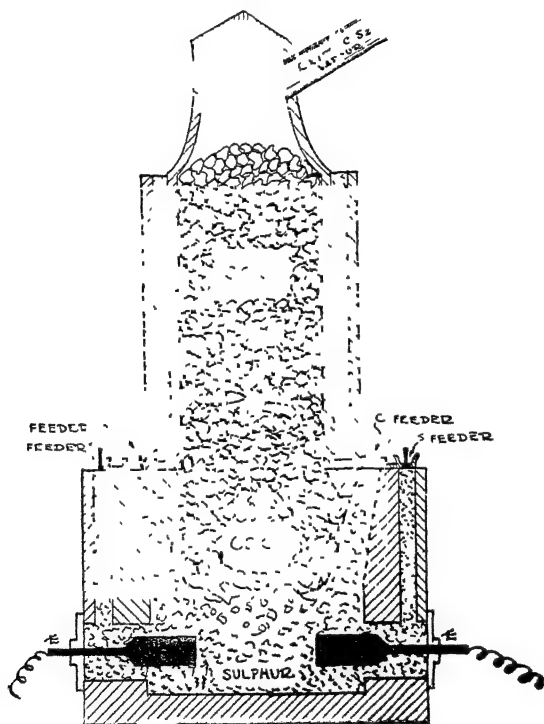


FIG. 79. Manufacture of Carbon Disulphide.

267. Physical Properties. Carbon disulphide is a colorless, mobile, highly refracting liquid. Its odor is strong and unpleasant unless chemically pure. Its specific gravity is 1.271 at 15° . It boils at 46.2° .

268. Chemical Properties. Carbon disulphide burns with a blue flame to carbon dioxide and sulphur dioxide. It is very inflammable, and flames should never be brought near the liquid. Mixed with oxygen it explodes when heated. A few drops in a jar of nitrogen dioxide will produce an exceedingly brilliant flame.

269. Uses. Carbon disulphide is used for vulcanizing rubber and as a solvent for rubber, fats, oils, phosphorus, sulphur, iodine, etc. It is also used for destroying prairie dogs, ants, mice and other pests.

270. Hydrocarbons and Their Derivatives. A hydrocarbon is a compound containing hydrogen and carbon, and of these compounds there are about 200 varieties which differ from each other in composition and properties. When we take into account the exceedingly large number of the compounds of carbon we must try to account for the reasons. It is generally explained by the following facts: (1) Different atoms of carbon can unite with each other. (2) Other atoms of entirely different elements can be introduced into the compounds either by addition or substitution. (3) The same atoms may have a different arrangement thus producing isomeric compounds which have different properties. (4) Carbon compounds may contain radicals in place of atoms. The first reason will be found to apply in the case of the simple hydrocarbons, while the others will be brought out more prominently in the derivatives.

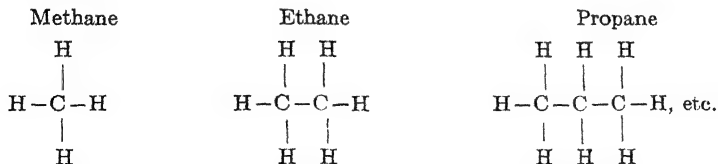
271. Classification of Hydrocarbons. For convenience the hydrocarbons are divided into several series according to the relation that exists between the number of carbon and hydrogen atoms in the compound. The first of these series is known as the "*Marsh-gas series*" because marsh-gas or methane is the first member and contains the smallest number of both carbon and hydrogen atoms. It is also to be noticed that the valence of the carbon is fully satisfied by the hydrogen atoms alone. The general formula for the members of the series is written C_nH_{2n+2}

where n stands for the number of carbon atoms. This may be seen by comparing the formulas of a few of the members of the series.

Methane, CH_4	Hexane, C_6H_{14}
Ethane, C_2H_6	Heptane, C_7H_{16}
Propane, C_3H_8	Octane, C_8H_{18}
Butane, C_4H_{10}	Nonane, C_9H_{20}
Pentane, C_5H_{12}	Decane, $\text{C}_{10}\text{H}_{22}$, etc

The names of the compounds are taken from the Greek numerals and up to $\text{C}_{24}\text{H}_{50}$ occur in regular order, after which they are irregular as high as $\text{C}_{60}\text{H}_{122}$, then none are known until $\text{C}_{120}\text{H}_{242}$ is reached. Of these the ones having less than 5 atoms of carbon are gases; those containing from 5 to 15 atoms of carbon are liquids, and all of the others are solids.

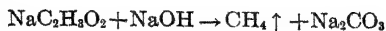
272. Homology. In studying the formulas given above it will be noticed that the increase in complexity is regular, each higher member having 1 carbon and 2 hydrogen atoms more than the member just below it. It is not, however, the simple addition of CH_2 to the molecule that makes the change, but rather the removal of one atom of hydrogen and the substitution of the radical CH_3 for this atom. This group is commonly called the methyl radical. A study of the structural formulas of some of the compounds will show how the atoms are thought to be arranged and how the radical is substituted for the atom. In all cases the valence of the carbon is taken as 4, while the valence of hydrogen is 1, the same as in the inorganic compounds.



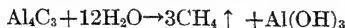
From the above it appears, and the theory is generally accepted that the carbon atoms have the power of uniting with

themselves. It is also evident that the methyl radical, CH_3 , can be substituted for an atom of hydrogen. This relation between the different members of a series is known as homology and the compounds are called homologous compounds. In writing the structural formulas of the organic compounds, i.e., in trying to show the arrangements of the atoms in the molecule, the written formula must be in one plane. It is believed, however, that the atoms in an organic molecule are usually in two or more planes. (See Fig. 51.)

273. Methane, CH_4 , often called marsh-gas or "fire-damp," will rise to the surface of stagnant pools when a stick is thrust into the ooze at the bottom of the pool. It is the product of vegetable decay and is found in abundance in mines, where it forms explosive mixtures with air. The mixture must contain from 3 to 85% of methane to be explosive. The products of the explosion are water and carbon dioxide. The explosive gases in mines are chiefly methane and carbon monoxide. The latter gas is called "white-damp" by the miners, and is not found as frequently as the dioxide, known as "black-damp" or "choke-damp." The most deadly gases responsible for more deaths than the explosions, are known as "after-damp," causing suffocation. That the after-damp contains an abundance of carbon dioxide may be seen from the fact that carbon dioxide is formed when both methane and carbon monoxide are burned. Methane is colorless, odorless, and slightly soluble in water, but is not acted upon readily by chemical reagents, though chlorine will gradually replace the hydrogen in diffused daylight. The gas may be made artificially by heating in a test-tube a mixture consisting of 2 parts of anhydrous sodium acetate with 3 to 4 parts of sodium or potassium hydroxide and 4 to 8 parts of quicklime or slaked lime and collecting the evolved gas over water. The reaction occurs between the sodium acetate and the hydroxide while the lime prevents the action of the hydroxide upon the glass.



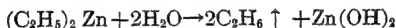
It may be formed by the action of water upon aluminum carbide,



or when hydrogen is passed over carbon and pulverized nickel, which acts as a catalytic agent. Its specific gravity is 0.5576 (air = 1). One liter of the gas weighs 0.716 gram.

Methane is the lightest compound gas known. It boils at -152° and solidifies at -186° . Its kindling temperature is 670° , upon which depends the efficiency of the Davy safety lamp. (See §48.)

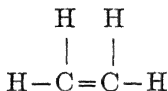
274. Ethane, C_2H_6 . This gas issues from the ground near some of the gas wells in oil regions. It may be reduced to a liquid that boils at -90° . Its specific gravity is 1.0494. One liter of the gas weighs 1.3567 grams. Its general properties resemble those of methane, but its flame is more luminous. It may be made in a number of ways. (1) By the electrolysis of acetic acid when the acetic radical at the positive pole breaks down into CH_3 and CO_2 , after which 2 methyl radicals, CH_3 , unite to form 1 molecule of ethane. (2) By dropping water cautiously upon cooled zinc ethyl.



Various other methods may be used. The union of 2 methyl radicals is called a synthesis.

275. The Olefine Series. Another homologous series of hydrocarbons having the general formula, C_nH_{2n} , is known as the olefine series, which theoretically should start with methylene, CH_2 , but no such compound is known and the lowest known member is ethylene, C_2H_4 , often called ethene or olefiant gas. Ethylene and its homologues form what is known as unsaturated compounds, because of their conduct towards halogens and halogen acids. When heated, ethylene combines with hydrogen to form ethane, but when heated alone, breaks up into various hydrocarbons. It combines directly with chlorine, bromine or iodine without loss of hydrogen, which

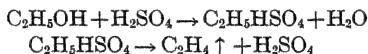
shows that the valence of the carbon is in part unsatisfied or that the compound is unsaturated. The evidence for the structural formula of ethylene is largely in favor of



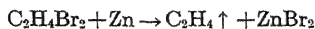
The difference between the consecutive members of the series, CH_2 , is the same as for the marsh-gas series, and the names of the members of the series follow in the same way, such as propylene, C_3H_6 , butylene, C_4H_8 , etc. The members of the series act as bivalent radicals, as might be assumed from a comparison with the marsh-gas series and the radicals derived from them

Can combine with 2 atoms	Can combine with 1 atom	Is saturated
Ethylene, C_2H_4	Ethyl, C_2H_5	Ethane, C_2H_6
Propylene, C_3H_6	Propyl, C_3H_7	Propane, C_3H_8
Butylene, C_4H_8	Butyl, C_4H_9	Butane, C_4H_{10}
Amylene, C_5H_{10}	Amyl, C_5H_{11}	Pentane, C_5H_{12}
(Pentene)		etc.

276. Ethylene, the only member of the series that we shall notice, is usually prepared by mixing ethyl alcohol with $1\frac{2}{3}$ times its volume of concentrated sulphuric acid and heating the mixture to about 175° . Ethyl sulphuric acid is first formed and this is decomposed into ethylene and sulphuric acid.

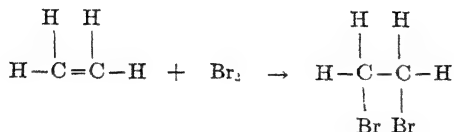


The gas is impure since ether is formed at lower temperatures and is mixed with the evolved gas. The pure gas may be prepared by warming an alcoholic solution of ethylene bromide with granulated zinc.

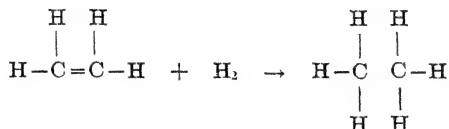


Other members of the series may be made in similar ways. The gas is colorless and has a sweetish odor. Its kindling tempera-

ture is 580° . It combines directly with chlorine or bromine yielding ethylene chloride, $\text{C}_2\text{H}_4\text{Cl}_2$, or ethylene bromide, $\text{C}_2\text{H}_4\text{Br}_2$, colorless oils of pleasant odor. The absorption takes place at the double bond in the following manner:

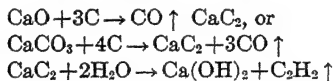


Ethylene can also be made to absorb hydrogen. The product is ethane,



277. The Acetylene Series. In the acetylene series the general formula is $\text{C}_n\text{H}_{2n-2}$. The lowest and best known member of the series is acetylene, C_2H_2 , or $\text{H}-\text{C}\equiv\text{C}-\text{H}$. The usual method of making the gas is from calcium carbide.

When calcium oxide or calcium carbonate is heated with carbon in an electrical furnace, calcium carbide, CaC_2 , is formed and this will react with water to form acetylene.



If the gas is passed into a solution of copper chloride in ammonium hydroxide, copper carbide, Cu_2C_2 , is formed and from this acetylene may be obtained by the action of dilute hydrochloric acid or potassium cyanide. Pure acetylene has an odor resembling garlic. It burns with a very luminous flame nearly white, and is not smoky if burned in a special burner. If burned in an ordinary burner the flame is very smoky. With $2\frac{1}{2}$ times its

volume of oxygen, acetylene forms a very explosive mixture. Acetylene has a specific gravity of 0.92 (air = 1). One liter of the gas weighs 1.162 grams.

278. The Benzene Series. This series has the general formula, C_nH_{2n-6} , and the simplest member is benzene, (or benzol) C_6H_6 , which is derived from coal tar. It is a colorless, strongly refracting liquid. At 0° it solidifies, the crystals melting again at 5.6° . It boils at 80.2° . It is insoluble in water, but will dissolve in alcohol and ether. When burned, the flame is bright and smoky. Benzene forms both addition and substitution compounds, an example of the former being hexachlorobenzene, $C_6H_6Cl_6$, or hexabromobenzene, $C_6H_6Br_6$, while monochlorobenzene, C_6H_5Cl , and monobromobenzene, C_6H_5Br , are ex-

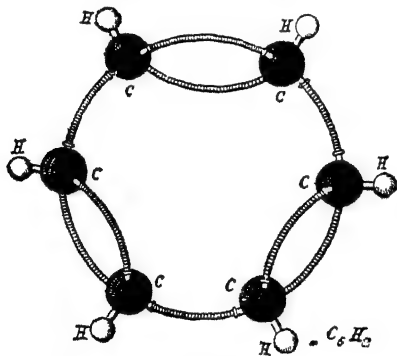


FIG. 80. The Benzene Ring.

amples of substitution compounds. Other substitution products will be spoken of in later sections. Much has been written on the theory of the structure of the benzene molecule. The formula is generally written as shown in Fig. 80.

279. Characteristics of Hydrocarbons as a Class. Hydrocarbons are neither acids, bases or salts, and do not act like these

familiar substances. They do not enter into double decomposition with acids, bases or salts, and in general do not react with chemical reagents. They all burn to water and carbon dioxide, and when heated without air may form either higher or lower members of a series. An interesting illustration is the splitting of the molecules of kerosene into gasoline by distilling under pressure.

Other Compounds of Carbon will be described in connection with the various topics discussed in the latter portions of the book.

280. Hydrocarbon Derivatives. Of the many derivatives of the hydrocarbons formed either by substitution or addition the most important and simplest are the following, together with the general formula, where R is taken to mean any radical consisting of carbon and hydrogen, as methyl, CH_3 , ethyl, C_2H_5 , phenyl, C_6H_5 , etc.

Form	Formula	Example	Formula
Alcohols and phenols	$\text{R}-\text{O}-\text{H}$	Ethyl alcohol	$\text{C}_2\text{H}_5\text{OH}$
Ethers	$\text{R}-\text{O}-\text{R}$	Ethyl ether	$(\text{C}_2\text{H}_5)_2\text{O}$
Aldehydes	$\text{R}-\text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{H} \end{array}$	Acetic aldehyde	CH_3CHO
Ketones	$\text{R}-\text{C}-\text{R}$ \parallel O	Dimethyl ketone	$(\text{CH}_3)_2\text{CO}$
Acids	$\text{R}-\text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{O}-\text{H} \end{array}$	Acetic acid	CH_3COOH
Halogen compounds	RCl , RBr , etc.,	Monochlorobenzene	$\text{C}_6\text{H}_5\text{Cl}$
Nitro compounds	$\text{R}-\text{NO}_2$	Nitrobenzene	$\text{C}_6\text{H}_5\text{NO}_2$

281. Problems.

- How much carbon dioxide will be produced by burning a diamond weighing one-half gram?
- How much carbon is required to reduce 12 grams of arsenic trioxide?
 $2\text{As}_2\text{O}_3 + 3\text{C} \rightarrow 3\text{CO}_2 + 4\text{As}$
- How much carbon monoxide may be obtained from the decomposition of 50 grams of oxalic acid? (§258).
- Write the quantitative equation for the reaction of carbonyl chloride and water. (§260).
- Write the quantitative equation for the explosion of "fire-damp."
 $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$
- Write the quantitative equation for the combustion of carbon disulfide.
 $\text{CS}_2 + 3\text{O}_2 \rightarrow \text{CO}_2 + 2\text{SO}_2$

TO FIND THE ATOMIC WEIGHT OF AN ELEMENT

The most important method of determining the atomic weight of an element is based upon the molecular weight of a series of gaseous compounds

containing the element, and the percentage composition of these compounds which is determined by analysis. Thus if we wish to determine the atomic weight of chlorine we first determine the vapor density of several gaseous compounds containing the gas. The molecular weight of the gas is found by multiplying the vapor density by 2. The percentage composition of the compounds is then determined by analysis. The actual weight of the chlorine in the compounds is then determined from the molecular weight and the percentage composition, by multiplying the two together and dividing the product by 100. The smallest weight of chlorine in any of the compounds is taken as the atomic, or combining weight of chlorine

In each of the following problems find the atomic weight of the element from the data given.

	Molecular weight	Percentage of element in compound
1	(a) 80	60
	(b) 100	48
	(c) 136	47.059
	(d) 60	53.33
	(e) 56	28.571
2.	(a) 80	40
	(b) 159	20.125
	(c) 136	23.529
	(d) 246	39.024
3.	(a) 101	38.613
	(b) 56	69.642
	(c) 65	60
	(d) 194	40.206
4.	(a) 106	43.396
	(b) 40	57.5
	(c) 58.5	39.316
	(d) 62	74.193

CHAPTER XIII

SULPHUR AND ITS COMPOUNDS

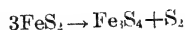
SULPHUR, SYMBOL, S. ATOMIC WEIGHT, 32.06.

VALENCE, 2, 4, 6.

282. Occurrence. Sulphur occurs both free and combined. Very large deposits are found in Louisiana, Sicily, Italy, Spain and Iceland, and smaller amounts are found in Japan, South America, and in a number of the Western States. Free sulphur is found near extinct volcanoes, and in the gases of active volcanoes sulphur occurs combined as sulphur dioxide or hydrogen sulphide. Many metallic sulphides are found, as copper pyrites, CuFeS_2 , lead sulphide, PbS , zinc sulphide, ZnS , ferric sulphide, FeS_2 , etc. Sulphates are also found in nature, some of the common ones being calcium sulphate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, known as gypsum, barium sulphate, BaSO_4 , called heavy spar, lead sulphate, PbSO_4 , etc.

283. Extraction of Sulphur. Former methods used almost entirely the primitive device of piling the sulphur in heaps, covering it with earthy matter and setting it afire. The air supply is limited and the sulphur burns in part, generating enough heat to melt the rest. The liquid sulphur is then drawn off and placed in horizontal cylinders of cast iron and vaporized. (Fig. 81.) The sulphur vapor passes into large rooms where it is condensed as it comes in contact with the cool walls of the rooms, forming flowers of sulphur. When the walls become too warm to condense the vapor, the sulphur condenses to a liquid on the floor of the chamber. This liquid is drawn off and is run into molds to form roll sulphur or brimstone. The Italian government forced the price of sulphur so high that new methods of extracting the sulphur from its compounds were devised, the

sulphides forming the basis of the process. Sulphides may often be decomposed by simple heating in closed vessels.



Sulphates are not used so extensively because of the greater difficulty to decompose them.

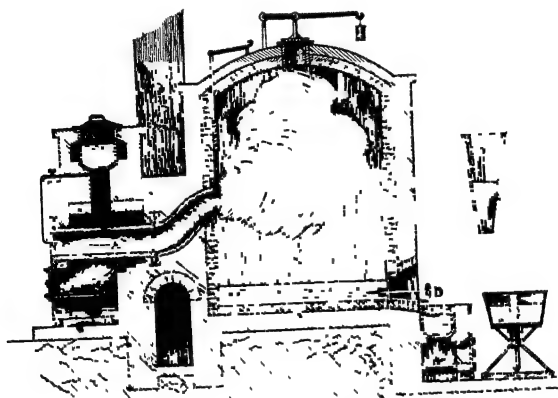


FIG. 81. Commercial Purification of Sulphur.

The Louisiana Sulphur Deposits occur at a depth of over 900 feet and are covered with quicksand, clay and rock. The problem of extracting the sulphur presented many difficulties, but was finally overcome by making borings in which were placed 3 pipes, one within another, reaching into the deposit of sulphur. (See Fig. 82.) Water heated under pressure to a temperature of about 170° is pumped down and comes in contact with the sulphur, which melts at 114.5° . After allowing sufficient time for the sulphur to melt, compressed air is pumped down through the small inner pipe, and when mixed with the sulphur lowers the specific gravity to about that of water, so that the mixture of air and sulphur flows up through the 3-inch pipe surrounding the air pipe. After exposure to the air in

large wooden vats, the sulphur quickly solidifies and for most purposes needs no other further purification. The Louisiana sulphur deposits are so extensive that they easily supply all the sulphur needed in the United States, while formerly practically all of the sulphur was imported from Sicily.

The Gulf Sulphur Co., in Texas, using the same process expect to mine 1000 tons of sulphur daily, with the use of 2000 barrels of fuel oil for heating 4,000,000 gallons of water daily.

284. Physical Properties.

Sulphur exhibits a great variation in general physical properties. It exists in at least three solid forms, two liquid forms and two or three gaseous forms. If a carbon disulphide solution of sulphur is allowed to evaporate, crystals known as right rhombic octahedra will separate. The specific gravity of these crystals is 2.05.

If sulphur is melted in a Hessian crucible and allowed to cool, monoclinic needles will be formed, having a specific gravity of 1.96 to 1.98. The rhombic form is stable below 96° and the monoclinic form is stable above that temperature so that either may be changed into the other form by changing the temperature. Since the ordinary temperature is far below 96° the rhombic is the more common form.

Sulphur at ordinary temperatures is a yellow substance, but at -50° it is nearly colorless. If sulphur is pure it is taste-

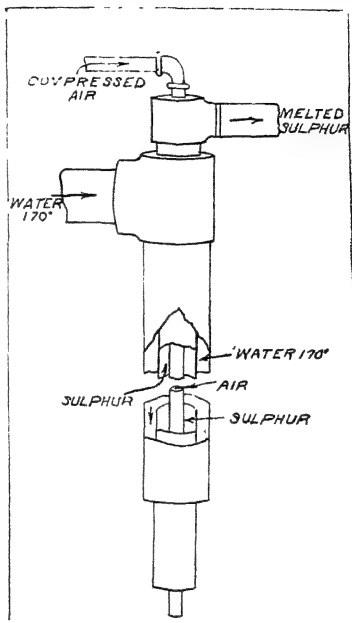


FIG. 82 Extraction of Sulphur in Louisiana

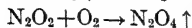
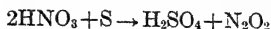
less and odorless. If heated in a suitable vessel sulphur melts at 114.5° to a thin straw colored liquid; at 200° to 250° it becomes thick and dark like molasses and cannot be poured from the vessel, but if heated still higher it again becomes thin and may be poured easily. If the sulphur is poured into cold water at this point, the amorphous, or non-crystalline, form is produced. This is soft and rubbery and has a specific gravity of 1.95. If allowed to stand, or if heated to 100° , or if chewed, it changes back to the rhombic form.

Sulphur boils at 448.4° and gives off orange yellow or red vapors, which at 500° have a density of 6.654 (air = 1) and at 1000° a density of 2.218, showing that the molecule contains $\frac{1}{3}$ as many atoms at 1000° as at 500° . Between these temperatures sulphur vapor is a mixture of S_8 , S_6 , and S_2 , the former decreasing and the latter increasing as the temperature is raised.

The best solvent for sulphur is carbon disulphide, of which 100 grams will dissolve 46 grams of sulphur, roll sulphur being more soluble than the flowers of sulphur. It is insoluble in water and only slightly soluble in alcohol and ether. It is, however, soluble in trichlorethylene, and since the carbon disulphide is very explosive, this non-inflammable substitute is being used more and more.

285. Chemical Properties. Sulphur belongs to the same chemical group as oxygen, but it is chemically less active than either oxygen or the members of the halogen group. (Chapter 11.) Sulphur combines directly with most metals, and directly, but not easily, with hydrogen. When heated in air it forms sulphur dioxide, SO_2 , which begins to phosphoresce, or glow, at 260° . Under proper conditions sulphur unites with three atoms of oxygen forming the trioxide, SO_3 . Sulphur unites with most acid forming elements, but the compounds are less stable than the corresponding oxygen compounds as may be seen by decomposing water and hydrogen sulphide by heat, the sulphide being decomposed at 400° , at which temperature the

steam from water remains unchanged. If sulphur is mixed with strong oxidizing agents it is oxidized to sulphuric acid.

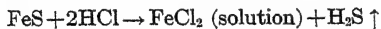


The action of sulphur on metals may be seen in the tarnishing of silver, especially where illuminating gas is used, since sulphur exists in the gas in the form of hydrogen sulphide, unless the gas has been carefully purified.

286. Uses of Sulphur. Sulphur is used extensively in the manufacture of sulphuric acid, gunpowder, fire works, and for vulcanizing rubber. In the form of sulphur dioxide it is used as a bleaching agent and as a germicide. As hydrogen sulphide, ammonium sulphide, or carbon disulphide, it is used extensively as a reagent and solvent in the laboratory.

HYDROGEN SULPHIDE, H_2S

287. Preparation. Hydrogen sulphide, sometimes called sulphydric acid, may be prepared by passing hydrogen over highly heated sulphur. The reaction is not complete as part of the gas is decomposed. The ordinary laboratory method is to pour some dilute hydrochloric acid upon ferrous sulphide.



The gas thus formed is (Fig. 83) impure and a better but more expensive, method substitutes antimony trisulphide, Sb_2S_3 , or aluminum trisulphide, Al_2S_3 , for the ferrous sulphide. The gas may be collected over warm water or by dry downward displacement.

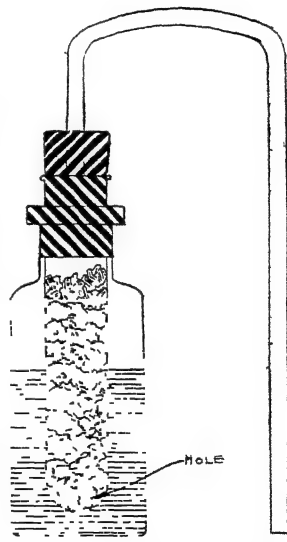
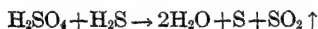


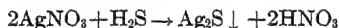
FIG. 83. Small Laboratory Generator for Hydrogen Sulphide.

288. Physical Properties. Hydrogen sulphide is a colorless gas having an odor of rotten eggs. Its specific gravity is 1.1895 (air = 1). One liter of the gas weighs 1.523 grams. It is soluble in water, 4.37 volumes dissolving in 1 volume of water at 0°, the solution being known as hydrogen sulphide water. It may be liquefied by a pressure of 17 atmospheres or by reducing the temperature lower than -60.4°, its boiling point. The liquid may be condensed to a white crystallized solid at -82.9°.

289. Chemical Properties. Hydrogen sulphide is a combustible gas, burning to water and sulphur dioxide if plenty of air is present, otherwise the hydrogen is burned first and the sulphur is deposited. It is decomposed at 400°, the decomposition beginning at 310°. Hydrogen sulphide gives up its hydrogen and acts as a reducing agent, so that it is decomposed by the addition of certain substances, such as the members of the halogen group, or bodies rich in oxygen, which remove the hydrogen. Sulphuric acid is reduced by hydrogen sulphide, the gas being oxidized at the same time. The equation for the reaction is



Hydrogen sulphide is easily decomposed by metals or the oxides of metals forming metallic sulphides. Certain metallic salts react with hydrogen sulphide, forming a sulphide and a dilute acid. The sulphide appears as a precipitate whenever it is insoluble in the acid, but if it is soluble it does not appear. Thus:



The following sulphides are insoluble in both water and dilute acids and hence may be precipitated as sulphides when hydrogen sulphide is passed into a solution of a salt of the metal: Silver, lead, mercury, bismuth, copper, cadmium, arsenic, antimony, gold and platinum, known as the hydrogen sulphide group. The following sulphides are soluble in dilute acids which are formed in the reaction, and insoluble in water, but since ammonium

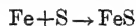
sulphide will produce ammonium compounds instead of dilute acids in the reactions, it is used to bring about precipitation: Iron, cobalt, nickel, manganese and zinc, to which are added aluminum and chromium, although the last two are precipitated as hydroxides instead of sulphides. The other sulphides are soluble in both water and dilute acids and, therefore, cannot be precipitated by either hydrogen sulphide or ammonium sulphide, but are produced by other methods: Calcium, strontium, barium, magnesium, potassium, sodium and ammonium.

Some of the other methods of producing sulphides are:

- (1) The reduction of a sulphate or a sulphite,

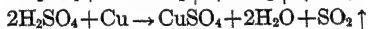
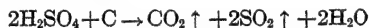


- (2) The direct combination of sulphur with a metal,



SULPHUR DIOXIDE, SO_2

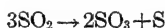
290. Preparation. Sulphur dioxide is formed when sulphur is burned in air, or in oxygen, or by the reduction of higher oxides or acids of sulphur by copper, charcoal, etc., or when a metallic oxide is heated with sulphur:



Sulphur burned in oxygen over mercury produces a volume of sulphur dioxide equal to the volume of oxygen taken.

291. Physical Properties. Sulphur dioxide is a colorless gas with a suffocating odor. If breathed in any quantity suffocation and death result. Its specific gravity is 2.2639 (air = 1). It may be liquefied by passing the gas through a tube surrounded by a mixture of ice and salt, or snow and salt. The liquid changes rapidly to the gas and in changing absorbs so much heat that a temperature of -60° is produced and some of the sulphur dioxide is solidified. The liquid boils at -10° . At 0° 1 volume of water will dissolve 79.9 volumes of the gas.

292. Chemical Properties. Sulphur dioxide neither burns nor supports combustion in the ordinary sense of the terms. Such substances as magnesium, potassium or finely divided iron, burn in the gas, and if it is heated with platinum in contact with air it is oxidized to sulphur trioxide. Under ordinary circumstances it extinguishes flame, a fact which is sometimes utilized to extinguish burning soot in chimneys. At 1200° sulphur dioxide decomposes



At lower temperatures it is very stable. Sulphur dioxide is the anhydride of sulphurous acid, which is formed when the gas is dissolved in water. The dry gas is not acid.

293. Uses. Sulphur dioxide in the presence of water is used to bleach cotton and linen goods, evaporated fruits, beet sugar, etc. It is used as a disinfectant and as a preservative, since it stops fermentation. It is used very extensively in the preparation of sulphuric acid.

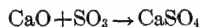
SULPHUR TRIOXIDE, SO_3

294. Preparation. Sulphur trioxide may be formed by passing sulphur dioxide and oxygen over finely divided platinum which may be in the form of platinized asbestos. A contact agent giving very satisfactory results for changing sulphur dioxide to sulphur trioxide is formed by treating finely divided lumps of kiesel-guhr or pumice with ammonium vanadate and then heating to drive off ammonia. The addition of a little sodium hydroxide or potassium hydroxide may improve its properties. Its efficiency is about 96%. Sulphur trioxide may also be formed by decomposing fuming sulphuric acid:



The acid is heated and the vapors are condensed in a receiver surrounded by a freezing mixture.

295. Properties. Sulphur trioxide is a white, crystallized solid, having a silky luster. It melts at 14.8° , forming a liquid that boils at 46.2° , but can be cooled to zero without solidifying. The vapor is colorless, having a specific gravity of 2.76 (air = 1). In contact with air sulphur trioxide produces white fumes of sulphuric acid by absorbing moisture from the air. Its combination with water produces a great evolution of heat and after the reaction is complete no water is present as water. This shows that the composition of sulphuric acid is similar to the hydroxides of calcium and magnesium, and the formula may be written $\text{SO}_2(\text{OH})_2$. Sulphur trioxide will unite with many metallic oxides to form metallic sulphates as



Sulphur trioxide is also known as sulphuric anhydride.

SULPHUR ACIDS

A great many sulphur acids are known, but the most important is sulphuric acid H_2SO_4 , sometimes called oil of vitriol. This with fuming sulphuric acid and sulphurous acid are the only ones that will be described.

SULPHURIC ACID, H_2SO_4

296. Preparation. The manufacture of sulphuric acid is essentially the oxidation of sulphur dioxide in the presence of water, the equation being



but the usual process is much more complicated than this. The formation of sulphur dioxide is simple, and so is the combination of sulphur trioxide with water to form the sulphuric acid, so that the problem in the manufacture of sulphuric acid is the *oxidation of the sulphur dioxide to the sulphur trioxide*. There are two methods used for this process which are so entirely different that they cannot both be used with the same apparatus. The first, and older, process is called

297. The Lead Chamber Process. Here the sulphur dioxide is first formed and then passed into a large lead chamber where it comes in contact with nitric acid and steam. The reactions that actually occur are complicated, but the main part of the change may be written



The nitrogen tetroxide then reacts with water



and the nitrogen dioxide reacts with the oxygen of the air to form more of the tetroxide which then unites with water as before. The nitric acid acts on the sulphur dioxide which is constantly admitted so that theoretically the process is continuous, leaving no residue, and possible with a very small amount of nitric acid originally admitted, but practically the problem presents many difficulties. (Fig. 84.)

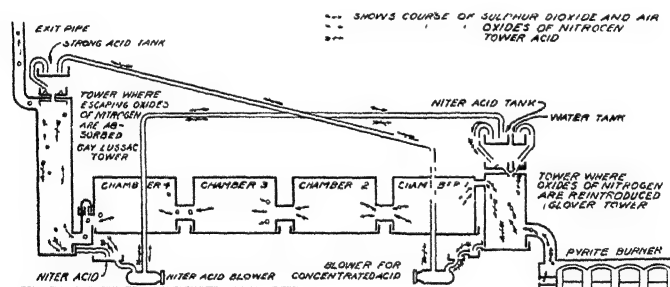


FIG. 84. Lead Chamber Process of Making Sulphuric Acid.

The acid thus formed has a specific gravity of about 1.5. It is then evaporated in lead dishes until it has a specific gravity of about 1.75, when it begins to act upon the lead, and it is then further evaporated in platinum, or in gold lined platinum, retorts, until the specific gravity is 1.842 to 1.854 at 0° if pure. (Fig. 85.) The commercial acid has a specific gravity of about

1.83 and always contains lead sulphate, from the lead dishes, and smaller amounts of nitrogen oxides, arsenic acid if arsenical pyrites were used for the sulphur dioxide, and certain other impurities.

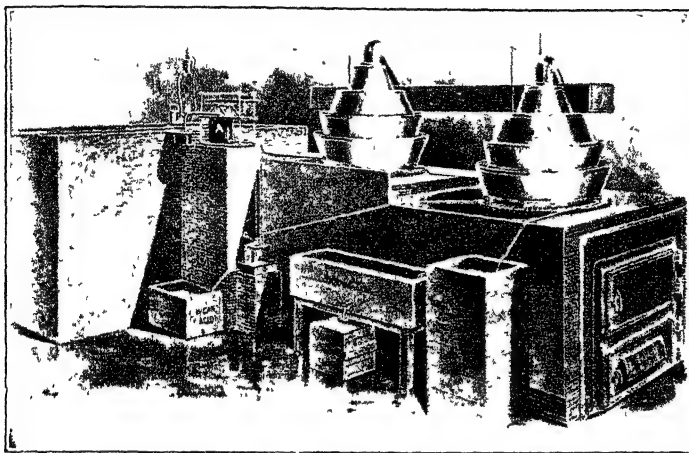


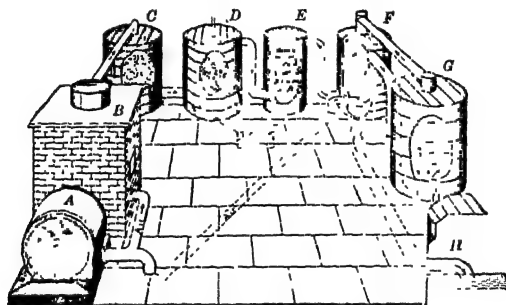
FIG. 85. Sulphuric Acid Concentrating Plant.

Sulphuric acid may be purified by distilling. The nitrogen products pass over with the first of the distillate which is rejected. Then the pure acid passes. The last part of the acid will contain the lead sulphate, arsenic acid, etc., and should not be distilled. Purification of sulphuric acid should not be attempted by a beginner, since explosions sometimes result, and the hot acid gives terrible burns. The distillation is conducted in a retort covered with an iron hood.

OTHER METHODS OF MAKING SULPHURIC ACID

298. (1) Contact Process. Since gold and platinum are very expensive and the lead chamber process is complicated, a later process, known as the contact process, is displacing the older method. In this process the sulphur dioxide is oxidized

to the trioxide, when in contact with finely divided platinum, and no nitric acid is used. The platinum acts as a catalyzer or contact agent and does not take part in the reaction. Theoretically it is exceedingly simple, but unless the sulphur dioxide is very pure the impurities soon clog the catalyzer and the reactions cease. (Fig. 86.) This process is superior to the other, as it does away with the large lead chambers, and all strengths of acid may be made in the same factory. The method has displaced some of the lead chamber factories.

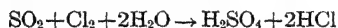


Contact process (diagrammatic)

A blower. B pyrites burner. C, dry scrubber filled with coke, D wet scrubber filled with coke wet with sulphuric acid. E, arsenic purifier. F heater. G, contact chamber. H, absorber (concentrated sulphuric acid)

FIG. 86. Contact Process of Making Sulphuric Acid

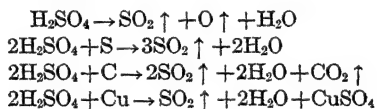
(2) A new process of manufacturing sulphuric acid heats a mixture of sulphur dioxide, chlorine and water vapor to 230° , and produces a mixture of sulphuric acid and hydrochloric acid in vapor form, as shown in the equation



This is cooled and practically all of the sulphuric acid is condensed in the form of finely divided suspended particles, and these are precipitated electrically to separate them from the hydrochloric acid. Sulphuric acid of 95% strength may be produced by this process.

299. Physical Properties. Sulphuric acid is a colorless, oily liquid, having, if pure, a specific gravity of about 1.842 measured at 12°. It always contains some water, but when this is reduced to a minimum the acid is solid at -34°. At 40° it emits fumes and does so until a temperature of 290° is reached, when, if water is present, it begins to boil. The water is boiled off first and the boiling point is 338°, when it is said to contain only one molecule of water in 12 molecules of the acid, making the formula $(\text{H}_2\text{SO}_4)_{12} \cdot \text{H}_2\text{O}$.

300. Chemical Properties. Anhydrous sulphuric acid loses its acid properties and acts as an oxidizing agent. If heated alone or with substances that act as reducing agents the acid is decomposed and the radical, SO_4 , is broken up, sulphur dioxide being one of the products.



Various metals that stand above hydrogen in the list of activity (See §36) will replace the hydrogen of dilute sulphuric acid and form metallic sulphates. (See §59.)

Sulphuric acid has a great affinity for water, with which it will combine with rise of temperature, the greatest rise in temperature being when 2 parts of the acid by volume are mixed with 1 part of water, the resulting temperature being 115° to 120°. It will combine with water in all proportions and seems to form compounds,



or tetrahydroxyl sulphuric acid, and



of hexahydroxyl sulphuric acid. The formula may be written $\text{S}(\text{OH})_6$ and the compound may be considered the normal sulphuric acid, since the greatest contraction in volume and

therefore the closest union occurs when the substances are thus mixed. Whenever the acid is to be mixed with water, the acid must always be poured slowly into the water with constant stirring so as to avoid sudden bursts of steam caused by overheating one part of the mixture. Dangerous explosions may occur if the water is poured into the acid. The affinity of the acid for water may be seen by exposing a known volume of the acid to moist air for 24 hours and measuring the increase of volume, which will often be found to reach 20%. If the acid is poured into a solution of cane sugar, $C_{12}H_{22}O_{11}$, the water is removed, and the solution turns black and swells.

• *Sulphuric Acid Forms Two Classes of Salts*, the normal sulphate, where all of the hydrogen of the acid has been replaced by the metal, and the acid sulphate, or bisulphate, where only half of the hydrogen has been replaced. The "bi" indicates that there is twice as much SO_4 in proportion to the metal as there is in the normal sulphates.

* **301. Uses of Sulphuric Acid.** Sulphuric acid is used in nearly all chemical industries, often in large quantities, such as in the manufacture of soda by the LeBlanc process, in the refining of petroleum, in the manufacture of fertilizers, nitroglycerine, gun cotton, water colors, etc. The extended use of sulphuric acid has resulted in a marked decrease in the cost, the first acid selling for about \$3.25 a pound, while normal cost of manufacture is about a cent per pound. About 5,000,000 tons are produced annually in the United States at this time.

302. Sulphurous Acid, H_2SO_3 , probably exists in solution when sulphur dioxide is passed into water since the solution is distinctly acid, turning blue litmus red, but it is not known in a free condition. It has great affinity for oxygen, hence reduces substances rich in oxygen, and is itself oxidized to sulphuric acid. It decolorizes potassium permanganate solution reducing it to potassium sulphate and manganese sulphate. The salts of the acid are called sulphites.

Sulphurous acid reacts with the active metals and will enter into double decomposition with bases and salts. When an excess of sulphur dioxide is passed into sodium hydroxide solution, sodium bisulphite and water are formed.



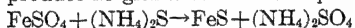
Sulphurous acid is used in paper manufacturing, for bleaching fruits, etc. As a preservative it is used chiefly in the form of sulphites.

303. Fuming Sulphuric Acid, $\text{H}_2\text{S}_2\text{O}_7$, is the ordinary acid to which sulphur trioxide is added. It is a light, brownish, oily liquid, fuming in air. It is decomposed on heating. It is used chiefly to dissolve indigo.

304. Problems.

1. How much silver sulphide is precipitated by the action of hydrogen sulphide upon two grams of silver nitrate in solution? How much hydrogen sulphide is required? What is the volume of the hydrogen sulphide in liters, and how much ferrous sulphide and hydrochloric acid should be used to produce it, all reactions being complete? §289, 287.

2. How much ferrous sulphate and how much ammonium sulphide should be used to produce 25 grams of ferrous sulphide?



3. Write the quantitative equation for the reaction of copper with sulphuric acid. (§290)

4. How much sulphur trioxide is required to make 100 kilograms of sulphuric acid?



TO FIND FORMULA WHEN THE PERCENTAGE COMPOSITION AND
MOLECULAR WEIGHT ARE GIVEN

The method of working these problems is the reverse of finding the percentage. Multiply the molecular weight by the percentage of the element; divide by 100 and the quotient gives the total atomic weight of the element; and this number, divided by the atomic weight of the element, gives the number of atoms of the element. Do the same for each element in the compound and combine as a formula for the compound. Use the nearest whole numbers as the number of each atom

Molecular weight	Percentage composition
1. 235	Ag, 45.96; I, 54.04
2. 127	Fe, 44.094; Cl, 55.905
3. 142	P, 43.66; O, 56.33

4.	246	As, 60.975; S, 39.024
5.	26	C, 92.308; H, 7.692
6.	271	Hg, 73.8; Cl, 26.2
7.	106	Na, 43.396; C, 11.320; O, 45.282
8.	101	K, 38.613; N, 13.861; O, 47.524
9.	56	K, 69.642; O, 28.571; H, 1.785
10.	63	H, 1.587; N, 22.222; O, 76.190
11.	136	Ca, 29.411; S, 23.529; O, 47.059
12.	100	Ca, 40; C, 12; O, 48
13.	194	K, 40.206; Cr, 26.804; O, 32.90
14.	60	H, 6.67; C, 40; O, 53.33
15.	46	C, 52.18; H, 13.04; O, 34.78

The teacher should assign other problems of greater difficulty from time to time. If the vapor density of a gas is given the molecular weight may be found by multiplying the vapor density by 2.

NOTE.

Chapter 24, showing the various attempts to arrange the elements, may be taken at this time.

CHAPTER XIV

PHOSPHORUS, ARSENIC, ANTIMONY AND BISMUTH

PHOSPHORUS, SYMBOL, P. ATOMIC WEIGHT, 31.04.

VALENCE 3 and 5

305. Occurrence. Phosphorus always occurs combined chiefly in bones as tricalcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, the amount of the tricalcium phosphate varying from about 65 to 86% of the bones, while the phosphorus obtained from the phosphate is only 8 or 9% of the weight of the bones. It also occurs in certain minerals, such as phosphate rock, and in the soil, from which it is absorbed in minute quantities by plants. Phosphate rock is used in the manufacture of artificial fertilizers and chemicals containing phosphoric acid. It is found in Florida, Tennessee, South Carolina, some of the Western States, Algeria, Tunis and elsewhere.

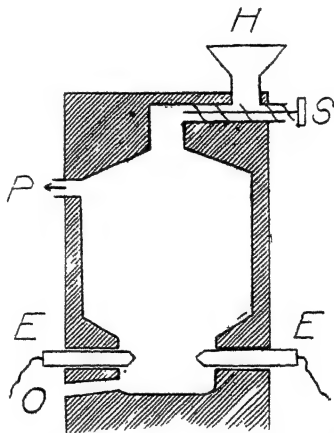
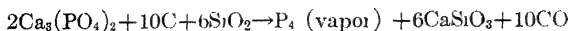


FIG. 87. Electric Furnace for Phosphorus

306. Preparation. Phosphorus is at the present time derived almost entirely from mineral phosphates, so that the older process of extracting phosphorus from bones by heating first with sulphuric acid and then with carbon and sand need not be described in detail. The *electrical process* is much more economical. Carbon, a phosphate and sand are thoroughly mixed and placed in a special electrical furnace and the electric current is passed through the mixture at the bottom. (Fig. 87.)

The mixture enters the furnace through the hopper **H** and the feed is controlled by the screw **S**. The current passes between the electrodes **E** and **E'**. The phosphorus passes out at **P** and the slag is drawn off at **O**. The changes that occur are



It is always impure and may be purified by straining it through chamois skin, by redistilling, or by treating it with chromic acid made from potassium dichromate and sulphuric acid, washing it with hot water and straining it through canvas bags. It is then rolled into sticks, somewhat resembling lemon candy, placed in bottles filled with water and packed in tin cans for market.

YELLOW PHOSPHORUS

307. Physical Properties. Ordinary phosphorus is a pale yellow, translucent, and waxy solid at ordinary temperatures, but brittle when cold. It melts when dry at 30° and under water at 44.2° , distilling at 290° . It is insoluble in water, but soluble in carbon disulphide, phosphorus trichloride, and slightly soluble in sodium hydroxide solution. Its specific gravity at 10° is 1.83. Its vapor density is 4.32 (air = 1) or 61.1 ($\text{H} = 1$). At ordinary temperatures and in solution the formula of the molecule is P_4 . At 1700° the molecule partially dissociates, forming P_2 .

308. Chemical Properties. Phosphorus takes fire in the air at 50° , or by friction, combining with oxygen to form phosphorus pentoxide, P_2O_5 . Under warm water, phosphorus and oxygen unite in the same way, a bright flash occurring whenever the stream of oxygen comes in contact with the phosphorus. Phosphorus burns in chlorine vapor to phosphorus pentachloride, PCl_5 , and in bromine vapor to the pentabromide, PBr_5 . When covered with iodine, phosphorus reacts forming a little phosphorus triiodide, PI_3 , and red phosphorus. Part of the iodine vaporizes, and the phosphorus burns to P_2O_5 . It

will combine directly with sulphur. At ordinary temperatures in the air, phosphorus combines with oxygen and glows in the dark, but this phosphorescence ceases in pure oxygen below 27° , unless the pressure is reduced.

309. The Effect of Phosphorus on the System. Phosphorus is a very active poison, either when breathed as a vapor or when swallowed, 0.15 gram being sufficient to cause death. It decomposes the bones of those who work with it continually, especially the jaw bone, the disease being called necrosis. When phosphorus burns the flesh, the wounds are very painful and very difficult to heal. The substance should, therefore, never be touched with the fingers, but must be held in tweezers and cut under water.

310. Red Phosphorus. This variety is the most important modification of the ordinary phosphorus. It may be formed by leaving ordinary phosphorus under water for a long time or by heating it to a temperature of 250° to 260° without air for some time. If heated in hermetically sealed tubes to a temperature of 300° , it is formed rapidly. A dark colored mass is formed which may be ground to a red brown powder having a specific gravity of 2.20. It sometimes contains a little yellow phosphorus which must be removed by washing with sodium hydroxide or carbon disulphide. Red phosphorus is almost the exact opposite of the ordinary variety, since it is not poisonous, does not melt at low temperatures, does not burn until heated to 260° , is insoluble in carbon disulphide, and is much less active chemically. If heated to 260° in the air, red phosphorus will burn, but if the heating is conducted in an atmosphere of carbon dioxide or nitrogen the red phosphorus will change to the yellow variety.

311. The following table shows a brief

COMPARISON OF YELLOW AND RED PHOSPHORUS

<i>Kind</i>	<i>Structure</i>	<i>Odor</i>	<i>Atoms in Molecule</i>	<i>Specific Gravity</i>	<i>Melting Point</i>	<i>Ignition Point</i>
Yellow	May be crystallized	Strong	4	1.83	44.2°	50°
Red	Amorphous	None	Not known	2.20—2.34	Does not Melt	260°

COMPARISON OF YELLOW AND RED PHOSPHORUS

<i>Kind</i>	<i>Boiling Point</i>	<i>In CS₂</i>	<i>In H-O</i>	<i>Effect on System</i>	<i>Is Kept</i>	<i>In the Dark</i>
Yellow	290°	Very Soluble	Insoluble	Very Poisonous	Under Water	Glowes Strongly
Red	Does not Boil	Insoluble	Insoluble	Not Poisonous	In ordinary Bottle	Not Visible

USES OF PHOSPHORUS

312. Matches. A little phosphorus is used for making pastes to exterminate vermin, but 90% of the product was formerly used for making matches. Both ordinary and red phosphorus are used for making matches, the first for common matches, the second for safety matches. In the ordinary match the paste containing the phosphorus is on the end of the match; in the safety match it is on the box. The paste for the ordinary match is usually made by stirring phosphorus into a warm solution of glue or dextrin. The oxidizing materials, such as lead peroxide, red lead, or manganese dioxide, are then added with the coloring material, which may be ultramarine, lead chromate, lamp black, etc. The paste is stirred until cold and the match sticks held in a frame, are dipped into the paste and are often coated with shellac to keep out the moisture. (Fig. 88.) The safety matches have for the paste sulphur or antimony trisulphide Sb_2S_3 , with potassium chlorate or potassium dichromate as the oxidizing material, though sometimes the same oxidizing materials are used as on the ordinary match. The paste on the box consists of red phosphorus, antimony trisulphide and dextrin or glue, to which powdered glass or emery is added to increase the friction. When the match is rubbed over the prepared surface some of the red phosphorus is converted by heat into yellow phosphorus which unites with a part of the oxidizing material on the box, developing enough heat to ignite the head of the match. Matches have been in use since 1827, when they

were first made in England from antimony trisulphide and potassium chlorate mixed into a stiff paste with water and gum. The manufacture and sale of matches containing ordinary phosphorus is prohibited by law in many countries and should be prohibited in all. Matches may be made by using phosphorus trisulphide, P_4S_3 , with lead oxide, PbO_2 , and paraffin. A mixture for making matches for out of door use consists of potassium chlorate, 1 part; potassium nitrate, 2 parts; lampblack, 60 parts; phosphorus, 60 parts; dextrin, 20 parts, covered with water-proofing material.

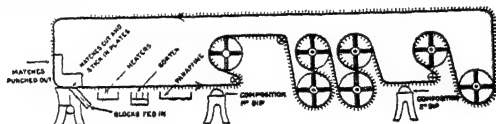


FIG. 88. Manufacture of Matches.

A Chinese patent for safety matches gives the composition of the head of the match as potassium chlorate 92 parts, oxalic acid 2 parts, antimony sulphide 14, powdered silicon dioxide 54, manganese dioxide 18 and glue 20. The igniting surface on the box is a mixture of antimony sulphide 92, barium sulphide 42, sulphur 15, red lead 33 and glue 18.

Figure 89 shows how we might get along without matches.

Phosphorus is now used quite extensively in making alloys, such as phosphor bronze. The phosphorus is introduced into the metal by melting it in a small retort placed above the melted metal and heated by it, with a bent tube extending from the retort to the lower part of the melted metal, so that the vapor of phosphorus passes up through the metal, combining with it to form the alloy.

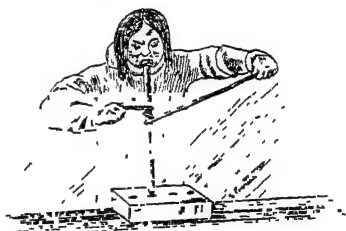
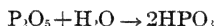


FIG. 89. Eskimo Fire Drill.

313. Phosphorus Pentoxide, P_2O_5 , is the only oxide of phosphorus important in elementary work. It is formed when phosphorus is burned in air or in oxygen, when it appears as a white smoke which will combine with cold water forming metaphosphoric acid, thus:



The equation for the reaction with boiling water is shown in §314. It is not decomposed by heat, is non-volatile, will absorb moisture from the air and is, therefore, often used as a drying agent.

314. Phosphoric Acid, H_3PO_4 , often called orthophosphoric acid, may be made by the action of nitric acid on phosphorus. The reaction is violent and dangerous with ordinary phosphorus, but safer with red phosphorus, though it should not be performed by a beginner. If phosphorus pentoxide is boiled with water, evaporated and held at 30° to 40° it is converted into orthophosphoric acid



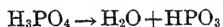
It may be formed by passing chlorine through warm water under which is melted phosphorus. The hydrochloric acid formed may be driven off by evaporation. If the remaining liquid is concentrated and cooled, crystals of phosphoric acid are deposited. They are deliquescent and soluble in water. The acid is tribasic and the salts of the acid are phosphates, having the general formula R_3PO_4 , where R is a univalent metal, as



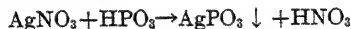
tri-silver phosphate being formed as a yellow precipitate. The most important compound containing the PO_4 group is $Ca_3(PO_4)_2$ found as phosphate rock. This is ground and mixed with sulphuric acid (Fig. 90) and sold as superphosphate as a fertilizer. Sometimes phosphoric acid is also added and the final product

is called double superphosphate. For a more complete discussion see Chapter 29.

315. Metaphosphoric Acid, HPO_3 , is formed when phosphoric acid is heated to about 400° in a platinum vessel, when 1 molecule of water is driven off.



It is formed when phosphorus pentoxide is dissolved in cold water (§313). Boiled with water to which a little nitric acid is added, it is reconverted to orthophosphoric acid. Its salts are metaphosphates, such as silver metaphosphate (white precipitate) formed when the acid acts upon silver nitrate.



Metaphosphoric acid is similar in composition to nitric and chloric acids, but differs from nitric since the latter is a strong, or highly ionized, and unstable acid, while the metaphosphoric is a weak, or slightly ionized, and stable acid. Very moderate heating decomposes nitric acid, but metaphosphoric acid may be heated to its boiling point, 550° , without decomposition.

ARSENIC. SYMBOL, AS. ATOMIC WEIGHT 74.96.
VALENCE, 3 OR 5.

316. Source and Preparation. Arsenic occurs both free and combined. Its chief compound is arsenopyrite, FeSAs , often

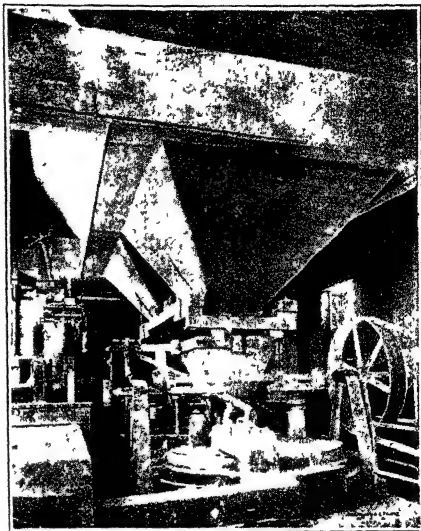


FIG. 90. Adding Sulphuric Acid to Phosphate Rock.

called mispickel. When this is heated it decomposes into FeS and As, ferrous sulphide and arsenic. The ore is heated in horizontal earthenware cylinders and the vapor condenses in sheet iron pipes. It is then distilled with charcoal in stone-ware retorts to purify it.

317. Physical Properties. Freshly sublimed arsenic exists as brittle, steel-gray crystals having a metallic luster. Their specific gravity is 5.73. Arsenic volatilizes without melting at 450° - 500° (Compare with iodine). Its vapor is yellow. Heated under pressure it melts to a transparent liquid.

318. Chemical Properties. When exposed to the air arsenic becomes covered with a brownish black layer, which is thought to be a suboxide of arsenic. Heated in the air or in oxygen, it burns with a bluish-white flame to form arsenic trioxide, As_2O_3 . The same reaction occurs when arsenic is thrown upon hot coals. Arsenic has no decided characteristics of its own, but acts both as a base forming and as an acid-forming element. Arsenic oxidizes slowly in water forming arsenious acid, which is soluble. Arsenic burns spontaneously in chlorine gas, forming arsenic trichloride, $AsCl_3$. The bromide, iodide and fluoride of arsenic may also be formed. Arsenic trichloride is a colorless, dense, oily, very poisonous liquid, having a specific gravity of 2.05, and boiling at 134° . When boiled with nitric acid it is converted into arsenic acid, similar to the way in which sulphur is oxidized to sulphuric acid, but in its general properties arsenic more nearly resembles phosphorus. Pure arsenic is not poisonous, but as it is almost always contaminated by its oxides, which are poisonous, it is very unsafe to taste it. Arsenic is used for hardening shot. (See §457.)

ARSENIC TRIOXIDE, As_2O_3

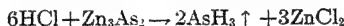
319. Preparation. Arsenic trioxide may be prepared by burning arsenic in air or in oxygen, but it is usually made by heating minerals that contain arsenic in contact with air. The

trioxide is condensed in horizontal chimneys or in a special building with communicating compartments through which the vapor must pass. It is condensed as a powder and is resublimed in cast iron pots and condensed in sheet iron cylinders. It is often called white arsenic.

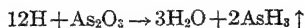
320. Properties. Recently sublimed arsenic trioxide is a vitreous amorphous mass, but it soon loses its transparency and changes to the crystalline form, which is opaque and resembles porcelain. The crystals occur in two forms, usually as regular octahedra, and more rarely as right rhombic prisms. One part of the opaque or crystalline variety dissolves in 80 parts of water, while one part of the amorphous will dissolve in 25 parts of water. The solution feebly reddens blue litmus, and gives a nearly tasteless solution of arsenious acid, which like sulphurous and carbonic acids, cannot be separated. Arsenic trioxide reacts with hydrochloric acid. It is reduced by heating with charcoal. It has a weak sweetish taste, and is a violent poison, although it is used to some extent in medicine. It is often taken, or administered to others, for the purpose of causing death. Tests for arsenic may be found in the Laboratory Manual. Of these, the most delicate are the Gutzeit and Gatehouse tests.

HYDROGEN ARSENIDE, AsH_3

321. Preparation. Hydrogen arsenide, or arsine, may be prepared by the action of hydrochloric acid on zinc arsenide, but is usually prepared in the laboratory by the action of ionic hydrogen on arsenic trioxide dissolved in hydrochloric acid. The reactions occur according to the equations



and



322. Properties. Hydrogen arsenide is a colorless, intensely poisonous gas having a penetrating odor resembling garlic. Hydrogen arsenide, like hydrogen phosphide, burns in the air

or in oxygen, the hydrogen first combining with the oxygen to form water, and then, if oxygen is plentiful, arsenic trioxide, As_2O_3 , is formed; if not, metallic arsenic is deposited. The metal will be deposited if the flame is cooled by pressing a dish into the flame or when a section of the delivery-tube is heated. (Fig. 91.) This is usually called Marsh's test for arsenic.

SULPHIDES OF ARSENIC

323. There are three sulphides of arsenic, As_2S_2 , As_2S_3 and As_2S_5 .

Arsenic trisulphide, As_2S_3 , may be made by a wet process by passing hydrogen sulphide into a solution of arsenic trichloride,



or by a dry process when arsenic and sulphur are fused together which gives a yellow powder, having a specific gravity of 3.459. It is both fusible and volatile. When made by the wet process the sulphide is insoluble in cold water, but is slightly soluble in hot water and is soluble in alkaline sulphides, forming sulpharsenites, which may be regarded as double sulphides in which the alkaline sulphide acts as the base and the arsenic trisulphide as the acid. When dis-

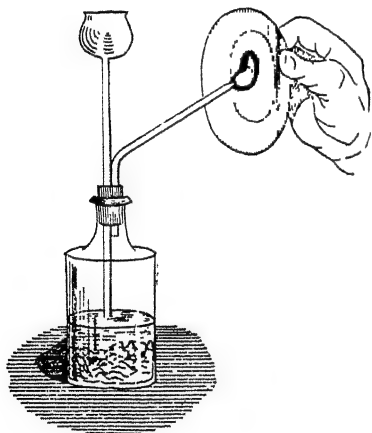


FIG. 91 Marsh's Test for Arsenic.

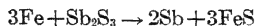
solved in caustic alkalis, an arsenite and a sulpharsenite are formed. Arsenic trisulphide is frequently called orpiment or King's yellow.

ANTIMONY. SYMBOL Sb. ATOMIC WEIGHT, 120.2

VALENCE 3 AND 5.

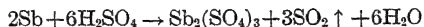
From its physical properties antimony would be classed with the metals: from its chemical properties, with the non-metals.

324. Occurrence and Preparation. Antimony is widely distributed and occurs as stibnite, Sb_2S_3 , which was known in antiquity. It comes largely from Hungary and Japan. The ore is mixed with iron with which it reacts to form ferrous sulphide, setting antimony free, which settles to the bottom, and may be drawn off.



325. Physical Properties. Pure antimony is a hard, brilliant, white, metallic substance with a bluish luster. Its specific gravity is 6.691. It melts at 630° and vaporizes at white heat. It may be crystallized by slow cooling and decanting the still liquid portion. Its vapor at 1640° shows its formula to be Sb_2 , while at lower temperatures Sb_4 is present.

326. Chemical Properties. Antimony acts both as a metal and as a non-metal, since it forms salts and enters also into acid radicals. Heated in the air antimony volatilizes and burns with a brilliant white flame to antimony trioxide, Sb_2O_3 . If melted antimony is allowed to fall upon glazed black paper, it breaks up into drops which run over the surface leaving dotted white lines. Powdered antimony burns in a jar of chlorine to antimony trichloride. It is soluble in aqua regia. With sulphuric acid, antimony sulphate, sulphur dioxide and water are formed.



With nitric acid it is oxidized to the trioxide or to antimonious acid, H_3SbO_4 .

327. Uses. Antimony is used in type metal, of which it forms 15 to 25%, while 10 to 20% is tin, the rest being lead. It makes the metal harder and thus permits sharper hair lines. It

is used in making Britannia metal, anti-friction metal, tartar emetic, etc. Powdered antimony is often rubbed upon plaster casts to give a dull metallic appearance.

328. Hydrogen Antimonide, or stibine, SbH_3 , is prepared in a manner similar to that for preparing hydrogen arsenide, by the action of ionic hydrogen upon a salt of antimony, as the chloride. The arsenic and antimony spots may be distinguished in several ways:

(1) The arsenic spots are brown and shiny while the antimony spots are black and smoky.

(2) The arsenic spots vaporize at a lower temperature.

(3) The arsenic spots are soluble in a fresh solution of sodium hypochlorite. The antimony spots are not.

(4) Hydrogen sulphide colors the arsenic spots yellow but gives a red color to the antimony spots.

OTHER COMPOUNDS

329. Chlorides. Antimony trichloride, SbCl_3 , known as butter of antimony, is formed by the action of hydrochloric acid on antimony trisulphide. It is solid, transparent and colorless, melting at 73° and boiling at 230° . It dissolves in hydrochloric acid, forming a colorless solution, but when diluted with water, a white precipitate of antimony oxychloride is formed having the formula, SbOCl . The trichloride should be added to the water for the best results. This reaction serves as a good test for the presence of water.

Antimony pentachloride, SbCl_5 , is formed when an excess of chlorine acts on the trichloride or on antimony. If powdered antimony is dropped into a jar of chlorine, a yellow liquid giving off abundant white fumes is formed. It cannot be distilled without partial decomposition into antimony trichloride and chlorine. The tribromide, triiodide, trifluoride and pentafluoride of antimony are known.

330. The Oxides are Sb_2O_3 , Sb_2O_4 , and Sb_2O_5 , the last being

formed when the metal is heated in nitric acid, which forms metantimonious acid, HSbO_3 , which, when heated to redness, loses water and forms the pentoxide. The trioxide is formed when antimony is heated in air. The tetroxide may be formed by heating the trioxide for a long time or by calcining the pentoxide.

331. Antimony Trisulphide, Sb_2S_3 , occurs in nature as stibnite, or may be made as an amorphous orange colored powder when hydrogen sulphide acts on antimony trichloride. It is insoluble in ammonium hydroxide, but dissolves in ammonium sulphide and the alkaline sulphides, and is reduced by hydrogen.

BISMUTH. SYMBOL, Bi. ATOMIC WEIGHT, 208.0
VALENCE 3.

332. Occurrence and Preparation. Bismuth is a true metal but is not abundant nor widely distributed. It occurs in veins of granite and clay slate as bismuth trisulphide, Bi_2S_3 , or as the trioxide, Bi_2O_3 . It is separated by roasting the ore in inclined tubes when the metal melts and runs out. The bismuth of commerce always contains some arsenic, sulphur, etc., from which it may be purified by heating once or twice with 1/20 its weight of potassium nitrate which oxidizes the foreign elements. From 150,000 to 190,000 pounds of bismuth are used in this country annually.

333. Physical Properties. Bismuth is whitish gray with a reddish tint. It forms rhombohedral crystals with a specific gravity of 9.83. It melts at 264° and the surface of the metal becomes oxidized and iridescent. Bismuth increases in volume and diminishes in density when it solidifies. It is volatile at white heat. If heated in an atmosphere of hydrogen it boils at 1600° .

334. Chemical Properties. Bismuth remains unaltered in the air at ordinary temperatures, but at a red heat it absorbs oxygen forming the trioxide, Bi_2O_3 . It is soluble in nitric acid

forming bismuth nitrate, $\text{Bi}(\text{NO}_3)_3$, which forms a basic nitrate when water is added. Hydrochloric acid will hardly dissolve it.

Sulphuric acid forms the sulphate. It is also soluble in aqua regia.

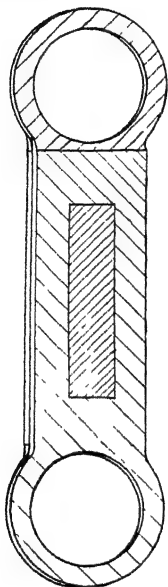


FIG. 92. Fusible Alloy Joint.

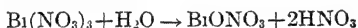
335. Uses. Bismuth is used in fusible alloys, for making safety plugs for boilers, chains for holding fire doors open (Fig. 92), or plugs for controlling automatic sprinkling systems. It is used in stereotyping and for solder. It has replaced lead to some extent in the cores of rifle bullets. Bismuth compounds are used in medicine, particularly the subnitrate and the sub-carbonate. The following table shows some of the typical

Alloy	BISMUTH ALLOYS		FUSIBLE METAL		Melting point C.
	Bismuth	Lead	Tin	Cadmium	
Newton's alloy	50 0	31 25	18.75		95°
Rose's alloy	50 0	27 10	22 9		100°
Darcet's alloy	50 0	25 00	25.00		93°
Wood's alloy	50 0	24 00	14 00	12 00	66-71°
Lipowitz's alloy	50.0	27.00	13 00	10 00	60°

See also Table 20.

336. Bismuth Compounds Similar to Antimony Compounds. Bismuth trioxide, Bi_2O_3 , formed by decomposing the nitrate by heat or by burning the metal in air, is a straw yellow powder fusible at red heat. It attacks clay crucibles. Bismuth tri-

chloride, BiCl_3 , formed when bismuth is burned in chlorine or when a stream of chlorine is directed against melted bismuth in a retort, was formerly called butter of bismuth. A crystallized hydrated chloride of bismuth may be made by dissolving the metal in aqua regia. The trichloride dissolves in hydrochloric acid and forms bismuth oxychloride when added to water. Another chloride of bismuth, Bi_2Cl_4 , has no analogues among the other members of the group. Bismuth nitrate, formed by dissolving bismuth in nitric acid appears as $\text{Bi}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$, which is very soluble in water acidulated with nitric acid. In pure water subnitrates are formed having formulas, BiONO_3 , $\text{Bi}(\text{OH})_2\text{NO}_3$ or $\text{BiOH}(\text{NO}_3)_2$.



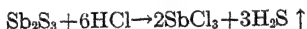
337. Problems.

1 Show how much phosphorus can be obtained from 75 kilograms of bones if the bones average 75% of calcium phosphate

2. How many liters of phosphine can be made from the action of 3 grams of phosphorus with sodium hydroxide?

3. How much hydrogen sulphide is required to react with 8 grams of arsenic trioxide?

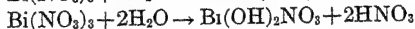
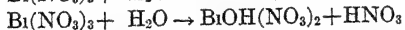
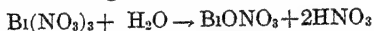
4 How much hydrochloric acid is required to react with 10 grams of antimony sulphide?



5. How much antimony oxychloride is formed when 5 grams of antimony trichloride in solution are poured into water?



6 Write the quantitative equations for the formation of the basic nitrates of bismuth according to the equations



TO FIND THE ATOMIC WEIGHT BY USING THE SPECIFIC HEAT

It has been found that the atomic weight of an element multiplied by its specific heat is approximately equal to 6.4. Conversely, 6.4 divided by the specific heat will give the atomic weight. Since the specific heat of a substance will sometimes vary with the temperature it will be found that

the results will not be absolutely rigid. The method serves a useful purpose by helping one to decide which of two possible atomic weights should be taken, as the one which found by the method of molecular weights, more nearly agrees with that found by the method of specific heat, is probably the correct weight.

1. The table showing specific heat is given in the back of the book, Table 17. From this table find the atomic weight of any metals as selected by the instructor.

2. From the table of common elements given in §21 find the specific heat of metals as selected by the instructor.

CHAPTER XV

BORON AND SILICON, GLASS MAKING

BORON, SYMBOL, B. ATOMIC WEIGHT, 10.9. VALENCE 3.

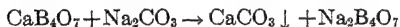
338. Occurrence. Boron occurs in nature as boric acid or as borates, of which the most important are sodium tetraborate or borax, calcium borate and a double borate of calcium and sodium. It occurs in different modifications such as the amorphous and adamantine forms.

At present there are no commercial applications of boron. The most important compounds of boron are borax, $\text{Na}_2\text{B}_4\text{O}_7$, chemically known as sodium pyroborate or tetraborate, and boric acid, H_3BO_3 .

339. Sodium tetraborate, or borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, is formed when boric acid reacts with sodium hydroxide or sodium carbonate. The radical B_4O_7 is the radical of tetraboric acid, $\text{H}_2\text{B}_4\text{O}_7$, which may be considered as boric acid minus water,



Calcium borate is a native compound in Nevada, California, Asia, etc., from which borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, may be derived by treatment with sodium carbonate.



A solution of borax is slightly alkaline. When heated to redness it loses its water forming a bead of transparent glass.

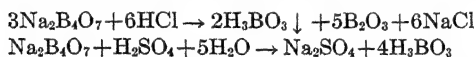


Borax is soluble in 17 parts of water at 25° , in 1 part at 80° , and in 0.5 part at 100° .

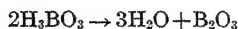
340. Uses. Borax combines with certain oxides of metals when heated, and is, therefore, used to test for certain metals.

(See §342.) Furthermore this property of combining with the oxides enables it to give a clean surface to metals, so that in soldering, the surface of the metal is first washed with a borax solution which causes the solder to adhere better to the clean surface. Zinc chloride and rosin are used for the same purpose. Some solder is made in the form of a hollow wire, packed with rosin. Borax is used in the manufacture of porcelain, as a preservative, to soften water, etc.

341. Boric Acid, H_3BO_3 , sometimes called boracic acid, an obsolete name, occurs free in many volcanic regions as in Tuscany, where the gases from volcanoes containing boric acid pass through water, thus dissolving the acid, which may be recovered by evaporating the liquid. Boric acid may be made from borax by the action of hydrochloric or sulphuric acid, which is added in small quantities until the liquid reddens blue litmus paper, when it is allowed to cool and crystals of boric acid separate. The final equations may be written as follows:



342. Properties. Boric acid occurs as pearly scales, greasy to the touch. They dissolve in 26 parts of water at 19° or in three parts at 100° . It is also soluble in alcohol. The taste of boric acid is faint, bitterish and somewhat acid. Boric acid is only slightly ionized, and is, therefore, known as a weak acid. It is so mild that it is used as an antiseptic wash for inflamed eyes. It has only a slight effect on litmus, turning blue litmus wine color. When boric acid is dissolved in alcohol and ignited it forms boric ether, $(\text{C}_2\text{H}_5\text{O})_3\text{B}$, and burns with a beautiful green flame. When heated, boric acid loses water forming boric oxide



Boric oxide thus formed is a transparent, glassy substance in which many oxides dissolve at redness, giving variously colored borates, thus serving as a test for metals. Borax does the same.

343. Some of the Colors Obtained with the Borax Beads are shown herewith:

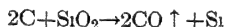
OUTER OR OXIDIZING FLAME		INNER OR REDUCING FLAME		INDICATES
<i>Hot</i>	<i>Cold</i>	<i>Hot</i>	<i>Cold</i>	
Amethyst to violet	Amethyst to violet	Colorless	Colorless	Mn
Green	Bluish green	Colorless	Brown to red	Cu.
Yellow	White	Gray or colorless	Gray or colorless	Zn.
Yellow to red	Colorless to yellow	Green	Bottle-green	Fe
Violet	Reddish brown	Gray	Gray	Ni.
Blue	Blue	Blue	Blue	Co.
Yellow	Grass-green	Green	Emerald-green	Cr.
Colorless	Colorless	Gray	Gray	Ag
Violet to blood-red	Brownish violet	Yellow	Bottle-green	Mn, Fe
Plum-color	Plum-color	Bluish green	Blue	Mn, Fe, Co.

344. Uses of Boric Acid. Boric acid is used chiefly as a mild antiseptic and to form borax beads.

SILICON. SYMBOL, Si. ATOMIC WEIGHT, 28.3.

VALENCE 4.

345. Occurrence and Preparation. Next to oxygen, silicon is the most abundant element, forming about one-fourth of the earth's crust. It occurs only in combination, either as silicon dioxide, SiO_2 , or as silicates of potassium, sodium, calcium, aluminum, etc., which are the most important constituents of all rocks except the limestones. Like boron, silicon exists in two forms, amorphous and crystalline. Amorphous silicon may be formed by fusing a mixture of sand and coke in an electric furnace, using less coke than for carborundum. (§346.)



Although silicon may be used in the thermit process, (§442), it is not otherwise very important as an element, and its properties will not be studied.

346. Silicon Carbide or Carborundum, SiC . When finely powdered sand is mixed with carbon and sodium chloride and the mixture subjected to the highest temperature of the electric

furnace (3500°), a reaction between the silicon of the sand and the carbon occurs as follows:

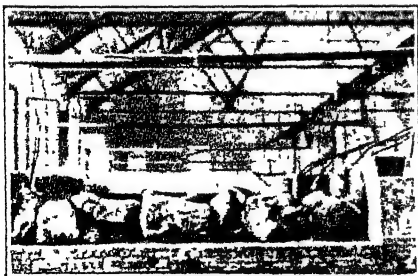
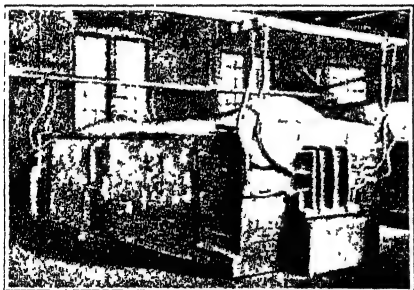
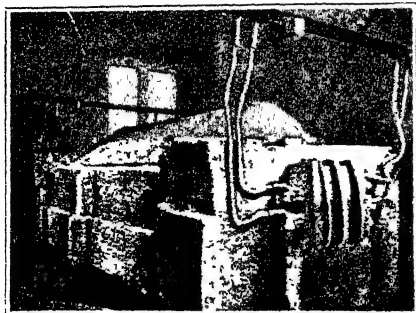
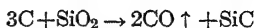


Fig. 93. The Manufacture of Carborundum.

In the commercial manufacture of silicon carbide a furnace having a capacity of 1,000 to 3,000 horse power is used. In a 1000 horse power furnace the electrodes are 10 inches in diameter and 40 inches long. The voltage varies from 125 to 160. Full voltage is used at the beginning and after 3 hours it is reduced to not over 100. The energy consumed is usually 22,500 kilowatt hours during an interval of 32 to 34 hours after which the current is shut off but the walls are allowed to stand 24 hours to prevent oxidation. (See Fig. 93.) The cost of production nearly doubled from 1915 to 1918.

Carborundum is extremely hard and, therefore, useful for grinding glass and other substances where diamond was formerly employed. Acids

do not affect it to any marked extent, but it is decomposed by strong alkalis. When powdered and heated in a stream of oxygen the carbon is burned out only with great difficulty. The most refractory variety of carborundum is unaffected by oxygen, ozone or sulphur at 1650° , and it is used for furnace linings. Carborundum is sold as carborundum paper, in the powder, as wheels, as knife sharpeners, etc. See Crystolon §444.

SILICON DIOXIDE OR SILICA, SiO_2

347. Occurrence. Silicon dioxide is found in quartz, flint, agate, and in a granulated form in sands and sandstones. As rock crystal it exists pure and crystallizes in six-sided prisms crowned at each end by six-faced pyramids. (Fig. 94.) *Sandstone* consists of grains of sand, SiO_2 , cemented together into a rock by cementing materials, such as calcium carbonate, iron oxide, silica or clay. The presence of iron causes a reddish color. Sandstones are usually soft and weather easily. In an amorphous condition it is found in such substances as opal and sometimes occurs as a deposit of powder. It is found in solution in the water of geysers and exists in the stems of plants. (Fig. 95.)

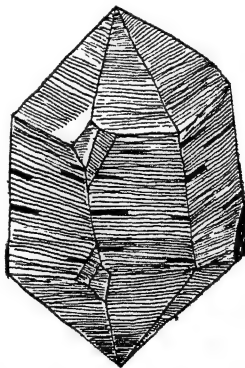


FIG. 94. A Crystal of Quartz.

348. Preparation. Silicon dioxide may be prepared by melting sand with sodium carbonate. The mass is dissolved in water; hydrochloric acid is added causing separation of silicic acid; it is then evaporated to dryness, moistened with hydrochloric acid and treated with water which causes the silicon dioxide to fall as a fine powder. It may also be formed by burning silicon.

349. Physical Properties. Pure silicon dioxide as found in

quartz crystals, has a specific gravity of 2.65, and is colorless or slightly colored by impurities. It is seventh in the scale of hardness. It melts only in the flame of the oxyhydrogen blow-pipe and may be reduced by charcoal in the electric furnace. It is insoluble in water, in boiling solutions of caustic alkalies and in all acids except hydrofluoric. Amorphous silicon dioxide such as flint, dissolves in boiling alkalies. Silicon dioxide does not expand when heated, making it valuable for chemical ware since the vessels made from it may be heated to redness and plunged into cold water without breaking, unless repeated

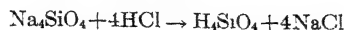


FIG. 95 Silica Mine.

too frequently. It is made into test tubes, crucibles, evaporating dishes, etc., and may be obtained as either the transparent or the opaque, the latter being much cheaper than the former. It is sold under several names, such as silica ware, fused mountain crystal ware, vitreosil, etc.

350. Chemical Properties. Hydrofluoric acid reacts with silicon dioxide forming water and silicon tetrafluoride. Fused with solid alkaline hydroxides or carbonates, silicon dioxide forms a glassy mass known as water glass which is an alkaline

silicate. If hydrochloric acid is added to a dilute solution of water glass or sodium silicate, the reaction, theoretically, gives silicic acid and sodium chloride,



but the acid loses one molecule of water becoming H_2SiO_3 , which is the usual formula for the acid. The sodium chloride may be removed by washing and when the silicic acid is heated all of the water is driven off and silicon dioxide remains.

Sodium silicate is described under the sodium compounds.

351. Uses of Silicon Dioxide. In addition to its use as laboratory apparatus, silicon dioxide finds many applications. Some varieties are used for ornaments owing to the impurities that are found in the crystals. Among the impure varieties are smoky quartz, rose quartz, amethyst, etc., or when the impurity undergoes change during the growth of the crystal, variegated crystals result giving jasper, agate, catseye, etc. Varieties known as chalcedony, opal and flint have water in combination. Rock crystal is used for optical lenses; infusorial or diatomaceous earth (Tripoli) is used in polishing powders and for removing the color from oils; kiesel-guhr for dynamite; sandstone for building, sand in making mortar, porcelain and glass.

352. Glass Making. Glass is an amorphous, usually transparent mixture of different silicates, one of which is always alkaline; the ones most frequently used being the silicates of sodium, potassium, calcium and lead. From its general behavior towards solvents in which, with the exception of hydrofluoric acid, glass is insoluble, and from its widely varying composition glass must be called a mixture and not a definite chemical compound. Most silicates and mixtures of silicates are difficult to fuse and after fusion crystallize, but the silicates used in glass making fuse easily, and have no sharply defined melting point; so that after fusion the mass becomes pasty before becoming rigid which permits its being blown and manipulated.

Glass is usually divided into two kinds, lime glass and lead glass. The materials used in lime glass are silica, an alkali and lime, while in lead glass, lead is substituted for the lime. Quartz sand is usually used to supply the silicon dioxide, quartz or flint being used for the finer grades. The alkali may be an alkali of sodium or potassium or both. The carbonate or sulphate is generally used, the carbonate fusing more easily while the sulphate is cheaper, but requires carbon to help reduce it. For lead glass sulphates are not used because lead sulphide would be formed which would darken the glass. The lime is usually chalk or limestone, or for finer grades pure marble dust free from iron, while for cheaper grades, less pure limestone and often some feldspar and granite are added. In lead glass the lead is added as litharge, PbO , or as red lead, Pb_3O_4 , the latter being preferred, but each must be free from copper. In addition to the above materials certain decolorizing substances are added such as manganese dioxide, arsenic trioxide or potassium nitrate.

The materials are melted in the "pot," which may be open as for lime glass, or closed as for lead glass. It is carefully constructed of the best quality

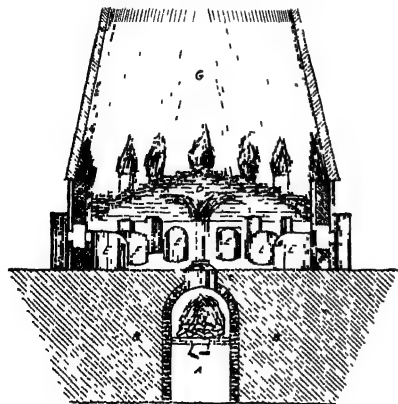


FIG. 96. A Glass Furnace.

of fire clay, the process of making and aging requiring several months. Before the pot is put into the regular furnace it is heated in a special furnace until it is as hot as the required temperature, and is transferred without cooling either the pot or the furnace to the interior of the furnace through the wall. (Fig. 96.)

It is then used continually without cooling until it wears out, the first charge being old glass to glaze the inside

and to prevent the solvent action of melted new materials. It is then charged with the new mixture or "batch" and old glass is added to make liquefaction easier and then the pot is filled with more batch until it contains the desired amount, and the decolorizing matter is added. Much carbon dioxide, sulphur dioxide, and oxygen escape and the alkali and other materials volatilize to some extent.

The reactions that occur are very complex and are not fully understood, and since different materials are used the composition of glass varies and is given by several different authorities as $2\text{Na}_2\text{SiO}_3$, $\text{Na}_2\text{Ca}(\text{SiO}_3)_2$ or $2(\text{Na}_2\text{O}, 3\text{SiO}_2)$, etc. After the glass melts it is allowed to cool until it becomes a homogeneous pasty mass after which it is manipulated according to the purposes for which the glass is to be used. It is then annealed in the annealing furnace to make it tough and less brittle. Annealing is simply slow cooling and may be conducted in various ways, one of which is to pass the glass through a long room on an endless carriage, the room being heated to a high temperature at the side where the glass enters and cool where the glass is removed.

Plate glass is usually a soda lime glass. The glass is poured upon a large cast iron casting table and rolled with a heavy iron roller, then annealed and ground to the required thickness and polished.

Window glass is always blown and is usually a soda lime glass. The glass is blown into a long cylinder open at both ends. It is cut lengthwise with a diamond and when placed in the annealing furnace softens and opens.

In cut glass the design is cut in the solid glass which has been given its shape by blowing or pressing. The cutting is done with a soft steel, copper or sandstone wheel whose cutting edge is fed with sand or emery and water. (Fig. 97.) Lead glass is usually used as it is softer and takes a better polish.

Pressed glass is made by the use of a die or mold and is very much cheaper than cut glass.

Variously colored glass may be made by adding different coloring matter to the batch. Green may be produced by adding potassium dichromate, chromium oxide, ferrous oxide, etc

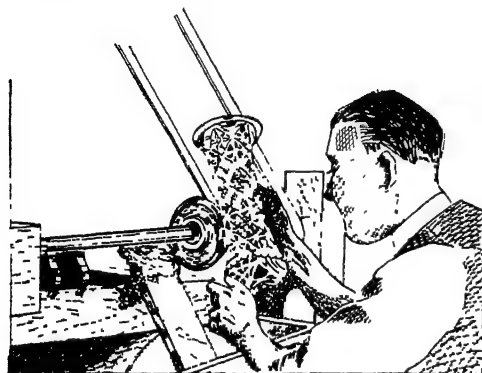


FIG 97 Cutting Glass.

Yellow is produced by sulphur or carbonaceous matter, cadmium sulphide, silver, etc. Blue is produced by cobalt oxide, cupric oxide, etc.; red by metallic copper, gold or cuprous oxide; white by adding cryolite or fluorite with feldspar to common glass; while black

glass contains pyrolusite, iron, etc. Various other colors may be made by appropriate coloring materials.

A working composition for glass for pressed tumblers is sand 100 pounds, soda ash 34 pounds, lime 12, sodium hydroxide 10, potassium nitrate 1, arsenic $\frac{1}{2}$, and manganese dioxide 5 oz.

Glass for electric light bulbs may be composed of sand 100 pounds, soda ash 30, lead tetroxide 35, lime 5, potassium nitrate 4, borax 2, manganese dioxide $\frac{1}{4}$ and arsenic trioxide $\frac{1}{4}$.

For manufacturing glass milk bottles a typical formula gives sand 2,000 parts, sodium carbonate 750, lime 250, sodium nitrate 21, manganese dioxide 16, powdered blue 2.

Non-breakable glass is now made by cementing a sheet of glass on each side of a sheet of pyralin. This does not decrease the transparency and the glass becomes tough enough to stand severe blows. It will crack when struck with a hammer but does not fall to pieces.

Very pure potassium carbonate is an essential raw material in the manufacture of optical glass which was produced in the

United States on a large scale during the war for search lights, reflectors, field glasses, and optical instruments of all kinds.

353. Problems.

1. How much hydrochloric acid will react with 15 grams of borax? How much of each of the products will be formed?
2. What would be the result if sulphuric acid were substituted for hydrochloric acid in the preceding problem?
3. Write the quantitative equations for the decomposition of boric acid by heat.
4. How much potassium will react with 18 grams of silicon dioxide?
5. How much silicon tetrafluoride will be formed by the action of 30 grams of silicon dioxide upon hydrofluoric acid?
- 6 Find the percentage composition of glass from the formulas

THE RATIO OF MOLECULAR WEIGHT TO SPECIFIC GRAVITY

Avogadro's hypothesis states that equal volumes of all substances in a gaseous condition, under the same conditions of temperature and pressure contain the same number of molecules. Based upon this law is the fact that the molecular weight of a gas divided by its specific gravity is a constant that approximates 28.88. Thus if either molecular weight or specific gravity is known the other may be found. $\frac{\text{Mol weight}}{\text{Sp. Gr.}} = 28.88$

1. If the specific gravity of a gas is found to be 0.967 what is its molecular weight?
2. If the specific gravity of a gas is found to be 1.524 what is its molecular weight?
3. If the specific gravity of a gas is found to be 1.178 what is its molecular weight?
4. If the specific gravity of a gas is found to be 0.971 what is its molecular weight?
5. If the specific gravity of a gas is found to be 1.27 what is its molecular weight?
6. If the molecular weight of a gas is 34 what is its specific gravity?
7. If the molecular weight of a gas is 123 what is its specific gravity?
8. If the molecular weight of a gas is 32 what is its specific gravity?
9. If the molecular weight of a gas is 160 what is its specific gravity?
10. If the molecular weight of a gas is 30 what is its specific gravity?

The results are only approximate and should be compared with results obtained by other methods that are more rigid.

TO FIND THE NUMBER OF ATOMS IN A SIMPLE MOLECULE

Divide the molecular weight by the atomic weight. These may be found by methods previously given. Some of the results are as follows:

Element	Molecular weight	Vapor density	Atomic weight	Number of atoms
Oxygen	32	16	16	2
Mercury	200	100	200	1
Arsenic	300	150	75	4
Hydrogen	2	1	1	2

The number of atoms sometimes varies with the temperature. Thus at 500° sulphur has six atoms to the molecule and above that temperature it has only two. Phosphorus, arsenic and antimony are said to have two atoms in the molecule at 1437°, while at low temperatures they have four. Zinc, cadmium and mercury have the atom and molecule identical, but the regular rule is two atoms to the molecule. The molecular weight of a gas is double the vapor density.

From the following data find the number of atoms in the molecule in each of the following problems.

	Vapor density	Atomic Weight
1.	62	31
2.	240	120
3.	32.5	65
4.	56.2	112.4
5.	96	32
6.	32	32

NOTE

At this point teachers may find it better for certain classes to select the work from the following chapters, instead of requiring the student to study the whole of each chapter.

Chapters XVI-XXII will complete college requirements. Chapters XXV-XXIII, XXX-XXXIII, XXXVII, XXXVIII and part of XXXIX may be used in household chemistry, or others may be selected as desired.

CHAPTER XVI

INTRODUCTION TO METALS

354. Occurrence. Certain metals, such as gold, silver, copper, bismuth, etc., occur free in nature but most metals occur combined with one or more of the following substances—oxygen, sulphur, chlorine, nitrogen, carbon, phosphorus, silicon, etc., as oxides, sulphides, chlorides, carbonates, sulphates, phosphates, silicates, nitrates, etc., from which the metal must be extracted by certain processes according to the nature of the metal and its combination. The largest number of metals are obtained from their oxides, sulphides or chlorides.

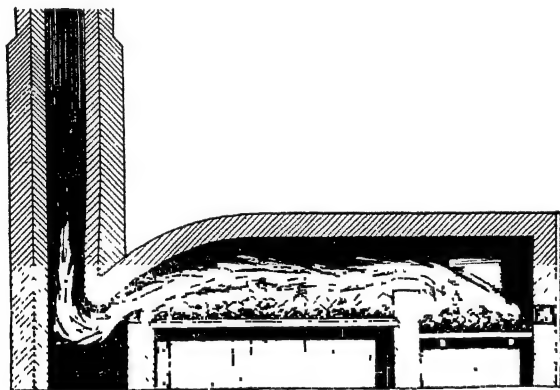


FIG. 98. A Simple Reverberatory Furnace.

355. Extraction. If the metal occurs as an oxide it may be obtained by fusing with carbon which unites with the oxygen forming carbon monoxide or carbon dioxide, according to the conditions. The blast furnace (Fig. 117) or the reverberatory furnace (Fig. 98) is usually used, but the high temperature of the

electric furnace must be used in some cases. On a small scale hydrogen is sometimes substituted for carbon as in the reduction of copper oxide. The thermit process (§442) is now used commercially for reducing a number of oxides, and the metal obtained is free from carbon.

If the metal occurs as a sulphide it is first roasted in air which causes the sulphur to pass off as sulphur dioxide and the metal is then in the form of the oxide which may be reduced with carbon. Sulphides are sometimes reduced by heating with iron (see §324). Sulphides are also treated by flotation, a comparatively new process applied to ores not rich enough to be handled otherwise, or to mixed ores to separate one from the others. Flotation may be applied to ores of copper, zinc, lead, iron, silver, gold, etc. The ground ore—not too fine—is mixed with water, sodium resinate and oil, sometimes with the addition of soap solution, sodium sulphide, sodium silicate or other material depending upon the ore to be treated. The liquid is then agitated producing a froth containing the sulphide of the metal.

Flotation is probably due to the occlusion and absorption of oxygen by the oil and the sulphide, both of which are oxidizable. In selective flotation a solution of soap and sodium silicate may be used in such proportion that a froth rich in one metal is first obtained. This is separated, the liquid diluted and reagitated to produce a froth rich in another metal. For the best results the ore should be freshly but not too finely ground. If a mixture of lead, zinc and silver ores is mixed with water containing bleaching powder and a small amount of frothing material, selective flotation of the lead occurs.

Oxidized ores such as copper oxide and copper carbonate may also be treated by flotation. The oil used in flotation depends partly upon the ore to be treated. With lead the best oil is eucalyptus, particularly with an acid pulp; followed by cresylic acid, hardwood creosote and lastly pine tar oils. After the froth containing the metallic sulphide is removed the material is concentrated and further treated to reduce the ore to a metal.

Chlorides may be reduced by heating with some metal as sodium, aluminum or magnesium which takes the chlorine forming a chloride of the metal used, while the metal that was formerly combined is set free.

Electrolysis is employed to reduce certain salts which are in a state of solution or fusion.

356. Physical Properties of Metals. Metals are those elements that are *good conductors of heat and electricity*, are *opaque* except when in very thin sheets such as gold leaf, have a certain *metallic luster* that does not disappear under the bur-nisher, but which does disappear when the metal is reduced to a very fine powder.

The *electrical conductivity* of a metal is the reciprocal of the resistance offered to the passage of the electric current. Thus if one metal offers twice as much resistance as another it has only half as much conductivity. The standard of resistance is the ohm which is taken as the resistance at 0° of a column of mercury 1 square millimeter in cross section and 1.063 meters long. The resistance of all metals increases as the temperature increases so that the resistance may be used to determine temperature.

Most metals may be *crystallized* under the proper conditions such as gold, silver, copper, lead, tin, etc.

Some may be *beaten or rolled* into thin sheets and are called *malleable*, such as gold and lead. In malleability the metals are arranged in the following order: Gold, silver, copper, tin, platinum, lead, zinc, iron and nickel. Gold leaf may be made so thin that it measures less than 0.0001 mm. in thickness. Arsenic, antimony and bismuth are brittle and may be reduced to a powder in a mortar.

Other metals may be drawn into *fine wires* and are called *ductile* as silver, copper and platinum. Those that are ductile are also tenacious, or capable of resisting the strain that tends to tear their molecules asunder. The tenacity of a metal is measured by the number of kilograms which a piece of the metal having a cross sectional area of one square millimeter can sustain

without breaking. The values are: Iron, 62; copper, 42; platinum, 34; silver, 29, gold, 27; aluminum, 20; zinc, 5; lead, 2. (See Table 19.)

Most metals are hard but sodium and potassium are soft. (See Tables 10 and 12.) Hardness is measured by the ease with which the substance may be cut. Caesium is the softest and chromium the hardest metal. Commercially hardness is measured by the Brinell hardness tester. This method is based upon the depth of the indentation made in the metal when a standard ball is pressed against it with a pressure up to 3000 Kg.

Most metals are solid at ordinary temperatures, but mercury is a liquid, except below -40° .

Most metals may be *melted* with comparative ease, but osmium will not melt in the oxyhydrogen flame which easily melts platinum, while an ordinary blast lamp will melt copper and many other metals. Those having a low melting or fusing point may be readily distilled while those with a high melting point can hardly be made to turn to a vapor. Some metals are volatile at moderate temperatures as mercury, 357° ; potassium and sodium, 700° ; cadmium, 770° ; zinc, 950° ; while others require the temperature of the electric furnace. (See Table 17.)

Some metals are *light enough to float* on water as sodium, potassium and lithium, and have great chemical energy, while others are heavy, as lead, gold and platinum, and are not active chemically, those having the lowest specific gravity being generally the most energetic. The specific gravity of the metals (water = 1) varies from lithium (0.59) to osmium (22.5). The light metals, potassium, sodium, lithium, calcium, magnesium, aluminum, strontium and barium have a specific gravity less than 5. The others are known as heavy metals. (See Table 13.)

Every metal has *certain properties*, either physical or chemical *which distinguish it from every other substance*, metallic or non-metallic, although many of them have several common properties. These facts are made the basis of analytical tests which first determine by the general properties the large group to which

the metal belongs, while the special tests that show the special properties determine which metal of the group we have. It is well to remember that the grouping for analytical tests is different from the grouping according to the periodic law.

357. Chemical Properties. The metals form compounds with each other and with the non-metals with varying energy. All metals unite with chlorine, forming chlorides, with oxygen forming oxides, and with sulphur forming sulphides. Some, such as magnesium and boron, unite with nitrogen forming nitrides, and most of them unite either directly with the more important acids to form salts or the salts are formed by methods such as are given in §§165 and 166.

358. Alloys. When metals combine with each other they are known as alloys. The combination does not always form definite chemical compounds since the metals will unite in almost any proportion so that in general they seem to be rather a solution of one metal in the other. The fusing point is not always as definite as in the case of a true chemical compound and is usually lower than the fusing point of any of the components. Several alloys are known that fuse below the boiling point of water so that they melt as wax when held in steam or hot water.

359. Amalgams. When a metal such as zinc, gold, etc., unites with mercury the alloy is known as an amalgam. The combination usually occurs easily at ordinary temperatures and is sometimes violent, as when sodium and mercury are combined even in small amounts.

360. Metallic Salts. Metallic salts may be grouped according to the nature of the radical with which the metal is combined. Generally an acid may be obtained that has the same general formula as the salt with the exception that hydrogen instead of a metal is combined with the radical. The most important metallic compounds are those that occur in the greatest abundance and have the widest application. Among these are chlorides, oxides, hydroxides, sulphides, sulphates, nitrates, chlorates, phosphates, carbonates and silicates.

CHAPTER XVII

ALKALINE METALS

SODIUM, POTASSIUM, AMMONIUM, AND LITHIUM

361. Comparison of Metals. Sodium, potassium and lithium resemble each other in many respects. They are all lighter than water, upon which they float and with which they react chemically, evolving hydrogen. When exposed to the air they tarnish rapidly and therefore must be kept under petroleum or other oxygen-free oil. They are known as the alkaline metals because they form strong alkalies when reacting with water.

Comparison of the metals of this chapter:

<i>Metal</i>	<i>At. Wgt</i>	<i>Valence</i>	<i>Specific Gravity</i>	<i>Melts</i>	<i>Boils</i>	<i>Color of Flame</i>
Li	6.94	1	0.534	186°	1400°	Red
Na	23.00	1	0.9712	97°	877.5°	Yellow
K	39.10	1	0.865	62.3°	667°	Violet

362. Comparison of Salts of the Alkaline Metals. The salts of the alkaline metals are *usually white, and most of them are easily soluble in water*. Some of the salts are highly colored, particularly some of the compounds of potassium and sodium, such as the permanganate, chromate, dichromate, ferrocyanide, ferricyanide, etc. In general the chemical action of the sodium and potassium salts is the same, but it is usually advantageous to use the sodium salts instead of potassium where the same action is secured, for the reason that the *cost of the sodium salts is less than that of the potassium salts*, and since the atomic weight of sodium is less than that of potassium *the percentage of the radical will always be higher when combined with the sodium*.

than when combined with potassium, thus *permitting the use of a smaller amount* to secure the same results.

363. Sodium. *Sodium is very widely distributed and abundant*, occurring chiefly in sodium chloride, sodium nitrate found in Chile, and in cryolite, in Greenland. It never occurs free. Sodium forms about $2\frac{1}{2}\%$ of the crust of the earth.

364. Preparation. Sodium was formerly prepared by the reduction of sodium carbonate by carbon in the form of charcoal or powdered anthracite coal when heated to about 1400° . It is now made largely by the electrolysis of fused sodium hydroxide, the electrodes being iron. (Fig. 99.) Sodium collects at the cathode in a collecting pot and is kept from mixing with the sodium hydroxide by a wire gauze. It is kept from oxidizing by the hydrogen that is set free at the cathode. The sodium is removed from time to time.

Sodium may be produced from salt by heating a mixture of 117 parts of sodium chloride with 80 parts of 80% pure calcium carbide to a temperature of 1200° to 1300° . This forms calcium chloride, sodium and carbon. The sodium may be separated by vaporizing and condensing.

365. Properties and Uses.

The action of metallic sodium upon water gives sodium hydroxide, which may be shown by phenolphthalein, producing a magenta color. The hydrogen, evolved at the same time, does not burn unless the water is

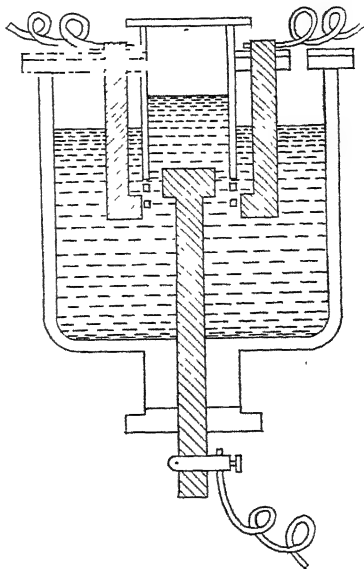


FIG. 99. Electrolytic Manufacture of Sodium

warmed. The decomposition frequently ends with a slight explosion, but this is violent if large pieces of sodium are used. Sodium has a bright surface that is easily tarnished in the air, and is, therefore, kept under petroleum, kerosene, or other oxygen-free oil. It was formerly used as a reducing agent to separate such metals as magnesium, aluminum and silicon from their chlorides, but it is not so important for that purpose since electrolysis has been so widely applied.

366. Sodium Chloride, or common salt, NaCl , is widely distributed either as deposits of rock salt or dissolved in the ocean water. If the salt is to be obtained from a salt deposit, water is pumped into the deposit, left until saturated, pumped out and evaporated, or if it is to be obtained from sea water the water is simply evaporated. The evaporation in all cases is conducted as far as possible without the aid of heat so as to cheapen the product. In hot countries the sun does a large part of the work. In cold countries the brine freezes and as the ice contains no salt it is removed from time to time until fire can be used with advantage. The brine is often allowed to trickle over bundles of twigs, thus exposing a larger surface to the air. When thus prepared, salt always contains sodium sulphate, calcium chloride and magnesium chloride, the last two causing it to attract moisture. Sodium iodate is also found in sea salt and is a desirable impurity, owing to its physiological action.

367. Properties. Sodium chloride crystallizes in colorless transparent cubes, often arranged as hollow pyramids or hopper-like masses. (Fig. 100.) A small amount of water is mechanically enclosed, but not as water of crystallization, and this water is given off when the salt is heated, causing a crackling sound known as decrepitation. Sodium chloride melts at 800° and volatilizes at redness. One part of salt dissolves in 2.78 parts of water at 14° and in 2.48 parts at 100° so that it is only slightly more soluble in hot water than it is in cold. A saturated solution boils at 109.7° , and at 8° has a specific gravity of 1.205. Salt is used for preparing many other sodium compounds.

368. Uses of Salt. In addition to its use as a condiment by men and animals, salt finds wide commercial application as a preservative and in the preparation of both metallic sodium and many of the sodium salts. A number of the important sodium compounds are made directly from salt, such as the sulphate, carbonate, bicarbonate, and hydroxide, while others are derived from the secondary products of salt, such as the phosphates made from the carbonate, the oxide and dioxide made from metallic sodium, etc. Sodium nitrate and sodium tetraborate

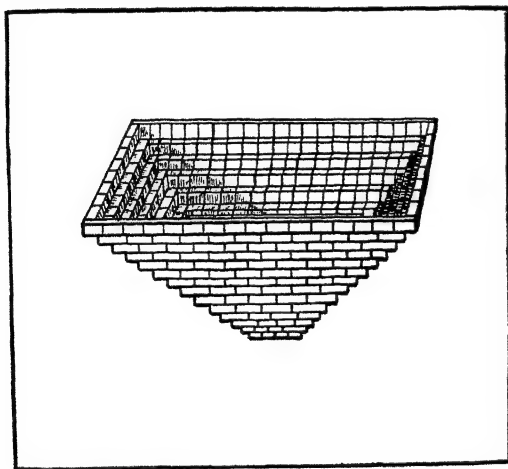


FIG. 100. A Crystal of Sodium Chloride.

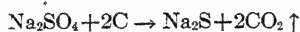
(borax) are found free in nature in large quantities, while sodium carbonate is found free to a smaller extent, but the chloride is the most important of all of the sodium compounds when the products made from it, either directly or indirectly, are considered. Nearly three and one-half million tons are used in the United States each year, and more than 15,000,000 tons in the world, with a value of over \$50,000,000. More than two-thirds of the salt produced in the United States comes from New York and Michigan, but the purest rock salt comes from Virginia. It contains 99.55% of sodium chloride.

369. Sodium Sulphate, Na_2SO_4 , known as Glauber's salt because first made by Glauber, is produced when sulphuric acid acts on sodium chloride at high temperatures in the manufacture of hydrochloric acid. It may also be made by the action of a concentrated solution of sodium chloride on magnesium sulphate. If the crystals of the salt are formed below 33° they contain 10 molecules of water, but between 33° and 40° they contain no water. The water is partly given off when the crystals are heated to 33° at which temperature the salt is most easily soluble, when 100 parts of water will dissolve 332.6 parts of the salt, while at 25° only 100 parts, and at 50° only 263 parts will dissolve in the same amount of water. When exposed to the air the sulphate effloresces (loses its water) and crumbles to a white powder. If the temperature is low in making the sulphate, the acid sulphate, NaHSO_4 , is formed. Sodium sulphate is used in medicine, in the laboratory for producing cold, in the manufacture of sodium carbonate, glass, etc.

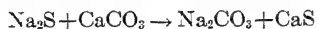
370. Sodium Carbonate, Na_2CO_3 , ranks next to the chloride in importance, being used in enormous quantities in making soap and glass and for washing purposes. It is the substance commonly called soda, or washing soda, and is found in small quantities in some parts of the world, as in Russia and California, but the larger amount used is made from sodium chloride, a process dating from the French Revolution, when Le Blanc invented his process after the supply of potash had been cut off from France. It was at one time derived from the ashes of sea plants, but is now made either by the Le Blanc process or by a later method, known as the ammonia or Solvay process, which is gradually displacing the older method.

371. Preparation. In the Le Blanc process the sodium chloride is first converted into sodium sulphate by sulphuric acid, the equation being the same as for the manufacture of hydrochloric acid when a high temperature is used. (§223.) The sodium sulphate thus produced is about 95% pure and is

known as the salt cake. The sodium sulphate is then changed into sodium sulphide by heating with charcoal,



and the sulphide is reduced by heating with chalk or limestone,



In practice the change from sodium sulphate to sodium carbonate is brought about by mixing 1000 parts of the sulphate with 1040 parts of calcium carbonate and 580 of coal. The mixture is then dried, put into a reverberatory furnace and thoroughly dried in compartment *b*. (See Fig. 101.) It is then transferred to compartment *a* where the intense heat of the flames, bent

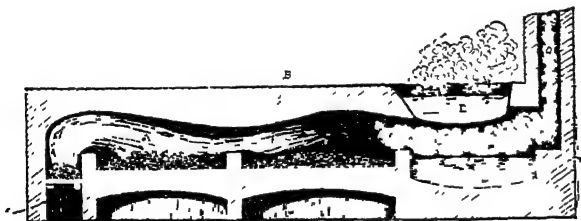
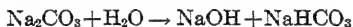


FIG 101. The LeBlanc Process of Manufacturing Sodium Carbonate

downward by the arched roof, brings about the reduction. The product, known as "black ash," contains from 37 to 45% of sodium carbonate. This is dissolved out with as little water as possible and the solution is transferred to compartment *d* where it is concentrated by the waste heat of the furnace. It is then drawn off into compartment *c* where it is evaporated to dryness giving "soda ash," $\text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$, which is dried by heat to drive off the water, thus obtaining the purified soda of commerce. When this is dissolved in water and crystallized, it forms large crystals, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, known as crystallized soda.

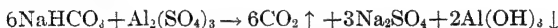
posed to the air for a while they lose their water and crumble to a white powder. Sodium carbonate is very soluble in water with evolution of heat, about seven parts of the salt dissolving in 100 parts of water at 0° and 45.2 parts dissolve if the water is at a temperature of 100°. The latter solution boils at 104.6°. It is used for cleaning. Sodium carbonate may be considered as being the product of a strong base, NaOH, with a weak acid H_2CO_3 . It is, therefore, strongly alkaline in its nature. When made into solution with water, the water is slightly ionized and reacts with the sodium carbonate, forming sodium hydroxide and sodium bicarbonate



373. Sodium Acid Carbonate, NaHCO_3 , commonly called sodium bicarbonate or baking soda, is formed when the normal carbonate is made by the ammonia process, or it may be made by passing carbon dioxide over the normal carbonate dissolved in its water of crystallization. It is less soluble in water than the normal carbonate, about 10 parts dissolving in 100 parts of water at 20° to 25°. It is salty in taste and slightly alkaline in its reactions. When mixed with an acid or an acid salt it gives carbon dioxide: It is used in baking and is known as baking soda. Baking powder usually consists of sodium acid carbonate mixed with an acid salt or an acid such as potassium acid tartrate (cream of tartar) $\text{KHC}_4\text{H}_4\text{O}_6$, or with tartaric acid, $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$, alum, etc. The carbon dioxide escapes and causes the dough to swell. Various other substances are used in baking powders, some of which are undesirable on account of forming insoluble or injurious compounds. When baking soda is heated alone it loses half of its carbon dioxide and is changed into the carbonate, so that if it is used alone in baking, or if too much is used for the cream of tartar the excess of baking soda yields the carbonate which produces a yellow color in the flour, with an unpleasant odor and an acrid taste. Sodium carbonate acts upon the gastric juice and interferes with the digestion. A solu-

tion of sodium bicarbonate is used in several types of fire extinguishers. (See Fig. 78.)

Instead of using carbon dioxide formed by the action of sulphuric acid upon sodium bicarbonate, a new method makes use of a preparation known as foamite. This consists of solutions of aluminum sulphate and sodium bicarbonate contained in separate tanks and mixed together just as they are played upon the burning surface, producing carbon dioxide as shown by the following equation.



The sodium bicarbonate contains an extract of licorice root. It does not take any part in the chemical reaction but the aluminum hydroxide formed as shown in the equation and the foamite when coming together produce a viscous mixture having a very low surface tension and when the carbon dioxide comes in contact with it a tough and durable foam is produced having a thick, creamy appearance. This cuts off the air supply and there is practically no transference of heat through the foam which does not soak in and injure the burning material. It is especially valuable in oil fires and has also proved effective for extinguishing fires in burning buildings.

374. Sodium Hydroxide or caustic soda, NaOH , is a white solid readily soluble in water with rise of temperature. The solution is strongly alkaline. Solid sodium hydroxide absorbs water and carbon dioxide from the air. It may be made by treating a rather dilute boiling solution of sodium carbonate with milk of lime.



The sodium hydroxide is decanted from the insoluble calcium carbonate and is evaporated in iron kettles until it becomes stiff. Some sulphides are present and these are oxidized either by blowing air through the mass or by adding sodium nitrate. It is also made by the electrolysis of sodium chloride solution,

the sodium reacting with the water after the chloride is decomposed so that the final equation will read



The sodium is formed at the anode and amalgamates with mercury, with which the floor of the apparatus is covered. (Fig. 103.) By rocking the apparatus the amalgam is brought into a central compartment where it is decomposed by the current after which it unites with the water to form the hydroxide.

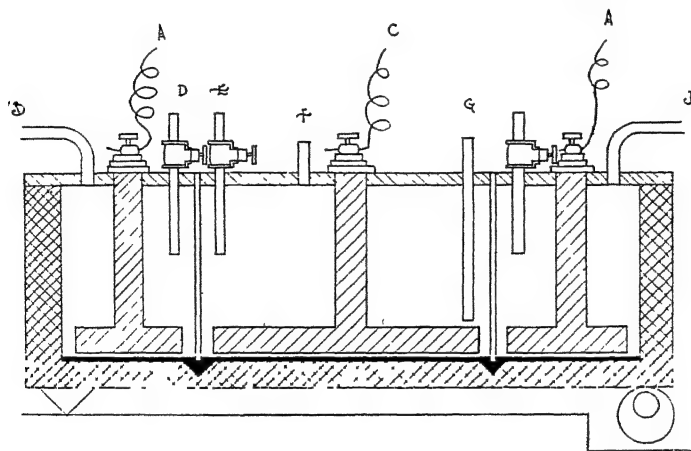


FIG. 103. Electrolytic Manufacture of Sodium Hydroxide.

375. Sodium Oxide, Na_2O , is a grayish solid formed when sodium is exposed to the air. **Sodium dioxide**, Na_2O_2 , formed by heating sodium in dry air to 300° , is often used as a bleaching agent and may be used to prepare oxygen. It is known commercially as "oxone." When thrown into water it decomposes in part yielding sodium hydroxide and oxygen. With acids it yields hydrogen peroxide. Oxone is used as the source of oxygen in the pulmotor, used for resuscitating persons overcome by gases or when nearly drowned. The oxygen is purified by passing it through water. See Fig. 13.

376. Sodium Nitrate, NaNO_3 , or Chile saltpeter, occurs in Peru and Chile, the deposits being called caliche. (Fig. 104.) It is a transparent crystallized solid largely used in making

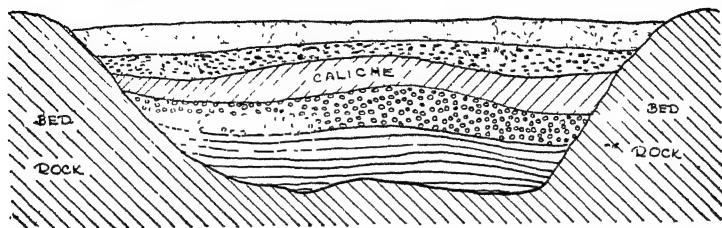


FIG. 104. A Bed of Sodium Nitrate, Known as "Caliche."

nitric acid and as a fertilizer. It cannot be used satisfactorily as a substitute for potassium nitrate in making gunpowder, since it does not decompose rapidly and attracts moisture from the air. (See Chapter 40). For the use of sodium nitrate as a fertilizer, see Chapter 29.

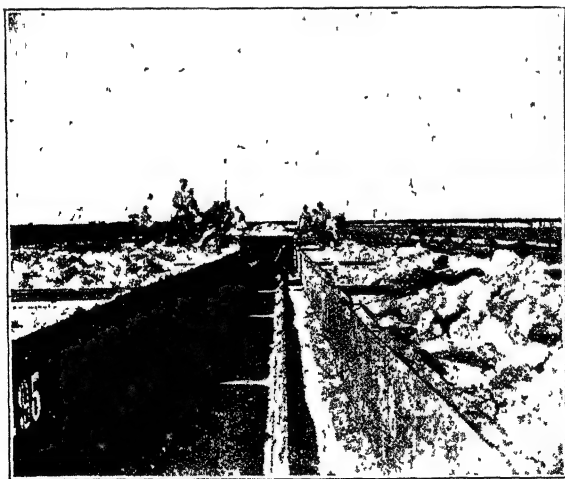


FIG 105. Mining Sodium Nitrate.

377. Sodium Phosphates. The most important and the most easily made phosphate of sodium is the secondary phosphate, or di-sodium phosphate, Na_2HPO_4 , which may be made by adding sodium carbonate to a solution of phosphoric acid until an alkaline reaction is shown; or it may be made by neutralizing calcium acid phosphate, obtained from bone dust and dilute sulphuric acid, with sodium carbonate. If a solution of the secondary phosphate is treated with an excess of sodium hydroxide and then evaporated, the tertiary, or normal phosphate, Na_3PO_4 , is formed. This salt dissolved in water has an alkaline reaction, while the mono- or primary phosphate, NaH_2PO_4 , is slightly acid.

378. Sodium Silicate, Na_2SiO_3 , is used chiefly in the form of an aqueous solution giving a yellowish or pale, greenish-yellow, viscous liquid, with a specific gravity of 1.3 to 1.4. It is strongly alkaline and is used for fire proofing, cementing stones, water proofing, in hydraulic mortars, cements, in dyeing and bleaching, as a filler for soaps, as an adhesive for labels and in a 10% solution as an egg preservative. It is commonly known as water glass.

379. Sodium Thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, called also the hyposulphite, or more commonly "hypo," is formed when sodium sulphite is boiled with sulphur. It occurs as white transparent monoclinic prisms, cooling and bitter to the taste. It is soluble in 0.65 volume of water at 15° and in 0.35 volume at 25° . When heated without water to 50° it melts in its water of crystallization, and may be kept as a solution until cooled far below its melting point. When cooling has proceeded sufficiently, or when a crystal of the salt is dropped into the solution crystallization occurs rapidly with evolution of heat, and a solid mass is formed. Sodium thiosulphate is used as an "antichlor" in bleaching (see §222) and paper making; as a fixing agent in photography (see §478) as a mordant for wool, as a disinfectant and in other ways.

POTASSIUM

380. Occurrence. Potassium occurs in nature only in compounds because the metal oxidizes so rapidly that it must be kept under naphtha. In combination it occurs in large quantities in many minerals such as feldspar, carnallite, sylvite, etc., with aluminum as a double sulphate known as alum, as potas-

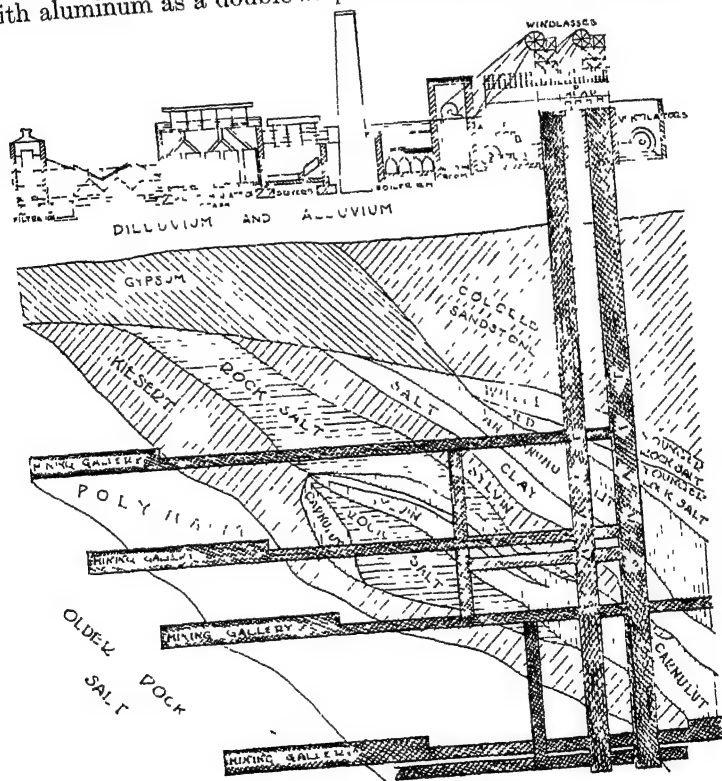


FIG. 106. Potassium Beds in Germany.

sium nitrate, known as saltpeter, in the ashes of plants chiefly as potassium carbonate, in the juice of grapes as potassium tartrate, and in various other forms. The most extensive deposits of potassium salts were once at Stassfurt. (See Fig. 106.) Owing

to their importance as a fertilizer the production of potassium salts is of vital importance. Germany before the war had practically a monopoly and claimed to be in a position to decide which nations could raise food and which must starve. (Fig. 107.)

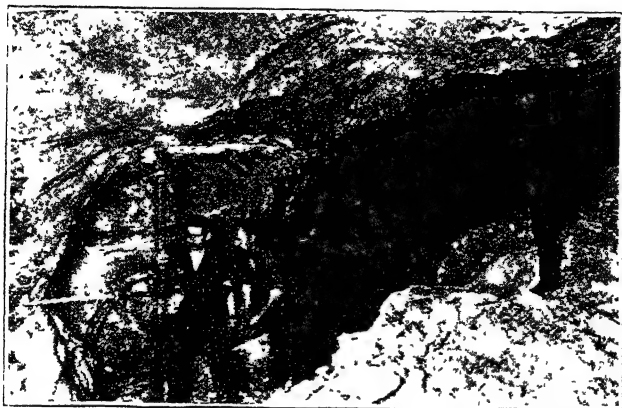


FIG. 107. Interior of a Potash Mine

In 1904 new beds of potassium salts of great purity—chiefly sylvite—were found in southern Alsace. There were 2 beds averaging 4 meters thick, covering 200 square kilometers and it was estimated that they contained about 325,000,000 tons of potassium salts, or enough to supply the world for 300 years. The output was controlled by the Kali Syndicate in favor of Stassfurt. The Stassfurt deposits are estimated at 84,000,000 tons.

It has been estimated that the entire earth to the depth of 1 meter contains 39,000,000,000,000 tons of potassium oxide, K_2O . As the rocks disintegrate the K_2O is washed out leaving an increased proportion of insoluble aluminum and iron silicates. Much of this K_2O finds its way to the ocean, which is estimated

to contain 440,000,000,000,000 tons corresponding to the removal of K_2O from the earth to the depth of about 11 meters and requiring at the present rate 6,000,000 years. (See §710.)

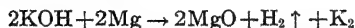
Kelp—a seaweed—contains potassium and from the grayish ashes obtained when kelp is burned from 30 to 35% of K_2O may be obtained.

One cement plant by precipitating the dust derived 1 ton of potassium sulphate per day since potash feldspar was used in making the cement.

In the same way the dust from blast furnaces may be precipitated by a Cottrell electrical precipitator and half of the 300,000 tons or more of the potassium salts charged into the blast furnace each year may be recovered. The average annual consumption of potassium salts in the United States from 1905 to 1914 was 198,636 tons, the maximum consumption of 279,780 tons, occurring in 1910. Other sources of potassium in the United States are the saline lakes of Nevada and California, beet sugar waste, molasses residue, wood ashes and potash bearing rocks.

It has been estimated that the wood ashes produced annually in the United States contain approximately 144,210 tons of potassium oxide. This is not all recoverable. Common wood ashes average about 3.6% potassium oxide but the percentage of wood carefully and completely burned runs from about 10% in some of the soft woods up to 35% in some of the hard woods.

381. Preparation. Potassium may be prepared by electrolysis after the manner of producing sodium; or from potassium chloride and calcium carbide, also similar to producing sodium as described in §364. It is also prepared by heating potassium hydroxide with magnesium,



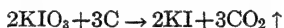
382. Properties. The chief physical properties of potassium were given at the beginning of this chapter. It is a soft, nearly white metal with a brilliant luster that disappears at once on

contact with oxygen of the air forming the oxide. In water potassium acts in a manner similar to sodium, but more violently, the heat generated being sufficient to ignite the hydrogen even in cold water. Potassium unites directly with chlorine and bromine with great energy. It may be used, therefore, to isolate magnesium and aluminum from their chlorides but other methods are used commercially.

383. Halogen Salts of Potassium. Potassium chloride, KCl, is the halogen salt of potassium that occurs in nature in large amounts. Any of the halogen salts may be made by neutralizing the proper halogen acid with potassium carbonate or potassium hydroxide. Potassium iodide, KI, is used in large amounts and may be made in several other ways such as the action of potassium hydroxide on iodine.

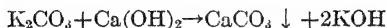


The iodate may be reduced by evaporating the water and heating the residue with carbon, as follows:—



The halogen salts of potassium are all soluble and crystallize in cubes. Their solubility is in the following order: potassium fluoride, potassium iodide, potassium bromide, potassium chloride, the latter requiring three parts of water for one of the chloride at ordinary temperatures. They are all decomposed by sulphuric acid. They are all capable of forming double salts, the double fluorides and double chlorides being the best examples, such as potassium platonic chloride K_2PtCl_6 . Potassium chloride is more soluble and more bitter than sodium chloride and produces a greater lowering of temperature. Potassium iodide is used in medicine and potassium bromide is used extensively in photography. Potassium iodide solution dissolves iodine readily. The solution is decomposed by nitric acid, iodine being deposited and red vapors being evolved if the solution is then concentrated. If starch paste is previously added it turns blue, thus serving to detect the potassium iodide.

384. Potassium Hydroxide, KOH, is made in the same general way as sodium hydroxide, using potassium carbonate instead of sodium carbonate.



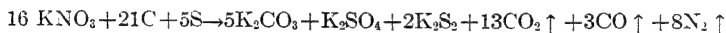
After the reaction ceases, the CaCO_3 is allowed to settle, the clear solution is decanted and evaporated. The residue is melted in a silver dish and cast in cylindrical molds. It is purified by dissolving in alcohol, is then distilled and fused in a silver dish. Perfectly pure potassium hydroxide may be made by the action of potassium sulphate on barium hydroxide solution. A solution of potassium hydroxide is formed which is decanted from the insoluble barium sulphate. Potassium hydroxide is now manufactured by the electrolysis of potassium chloride, in a manner similar to that used for sodium hydroxide. Chlorine is liberated at the anode, hydrogen and potassium hydroxide at the cathode. These products must be kept separate or potassium hypochlorite and potassium chloride will be formed. The cell is divided by a partition of asbestos placed either vertically or horizontally, the electrodes being placed in a similar position. The anode is made of graphite to resist the chlorine while the cathode is made of iron to resist the alkali. Pure brine flows in continuously at one part of the cell while potassium hydroxide and undecomposed potassium chloride flow out from another part.

Properties. Recently fused potassium hydroxide is a white, opaque solid, denser than water in which it is very soluble forming a very powerful alkali. It absorbs water and carbon dioxide from the air becoming potassium carbonate. It rapidly corrodes animal tissues which form a clear solution when boiled with the hydroxide. It is often used for making soft soap, but sodium hydroxide is used wherever possible because it is cheaper,

385. Potassium Nitrate, KNO_3 , known as niter or saltpeter, occurs in many localities, but is more common in southern climates. It may be made from sodium nitrate by adding to its

solution a solution of potassium chloride. The mixture is then boiled and the sodium chloride crystallizes and is separated when hot; the potassium nitrate when cold. It is formed when potassium hydroxide is neutralized with nitric acid.

Properties. Crystals of potassium nitrate are similar in shape to the crystals of pure silica. See §347. They are very soluble in hot water of which 100 parts dissolve 246 parts of the salt at 100°, but only 13.33 parts at 0°. The taste of the solution is salty and cooling. Potassium nitrate melts at 341°, and at higher temperatures gives off oxygen and is reduced to the nitrite which is decomposed at red heat. When thrown upon red hot coals the nitrate melts, decomposes and increases combustion. This is known as *deflagration*. The nitrate meanwhile becomes the carbonate. Ordinary black gunpowder is a mixture of 75% of potassium nitrate, 15% of charcoal and 10% of sulphur. The equation for the explosion of gunpowder has been written thus.

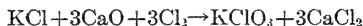


A discussion of smokeless powder and other explosives may be found in Chapter 40.

386. Potassium Chlorate, KClO_3 , is formed when chlorine acts upon a concentrated solution of potassium hydroxide or potassium carbonate.



It may be formed by the action of chlorine on a mixture of lime and potassium chloride in water, where the final equation is



It may also be formed by the electrolysis of potassium chloride. Potassium oxide is formed and this unites with chlorine to form the chlorate, which is purified by recrystallization.

Properties. Potassium chlorate forms monoclinic crystals having a salty taste. It begins to melt at 372° and gives off one third of its oxygen forming the perchlorate and the chloride.

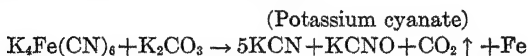
Above 400° the perchlorate is decomposed forming the chloride and evolving the rest of the oxygen. The chlorate deflagrates when thrown upon hot coals. It explodes when rubbed with sulphur, and is dangerously explosive when rubbed with phosphorus. It is soluble in water, 3.3 parts dissolving in 100 of water at 0°, six parts dissolving in the same amount at ordinary temperatures, and 56 parts at 100°. It is used in medicine for throat affections, and is used largely for making matches, explosives, fireworks, etc.

387. Potassium Carbonates. Potassium normal carbonate, K_2CO_3 , is a white powder that may be made by pouring water upon wood ashes, evaporating the solution and calcining the residue in the air. It is known as potash, or if pure as pearl ash, and is used in the manufacture of hard glass, soft soap and potassium compounds. It may be made in other ways, such as the treatment of potassium chloride in a manner similar to the treatment of sodium chloride, for the formation of sodium carbonate. It is very soluble in water and shows an alkaline reaction. The acid carbonate, $KHCO_3$, is made by passing carbon dioxide into a solution of the normal carbonate. It is less soluble than the normal carbonate, is alkaline and gives off carbon dioxide when boiled.

388. Potassium Cyanide, KCN, is a poisonous white solid soluble in water, formed when potassium ferrocyanide is heated.



If potassium carbonate is added it reacts with the last two products in the form of ferrous cyanide, $Fe(CN)_2$, forming ferrous carbonate, $FeCO_3$, and two more molecules of the potassium cyanide, so that the final equation is



Potassium cyanide unites with other cyanides to form double cyanides. It is used in analysis, in metallurgy, and in electro-

plating, although sodium cyanide is being used more every year.

389. Potassium Ferricyanide, $K_3Fe(CN)_6$, when dissolved and mixed with a solution of citrate of iron and ammonia is used as a coating on unsized paper for blue print paper. When this paper is exposed to the light and washed with very dilute hydrochloric acid, a coating of Prussian blue will be left on it. Potassium salts, like sodium salts are very numerous and widely used.

AMMONIUM SALTS

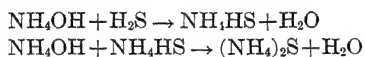
390. Metallic Ammonium, NH_4 , is not known, but there are a number of important salts whose composition indicates that NH_4 is capable of reacting as a metal, but all attempts to isolate it have failed. Ammonium amalgam may be made by adding a concentrated solution of ammonium chloride to sodium amalgam, but it cannot be separated from the mercury as ammonium. The ammonium salts are all characterized by their great volatility and the ease with which they decompose when heated, especially when mixed with a caustic alkali, such as calcium hydroxide, $Ca(OH)_2$; potassium hydroxide, KOH ; or sodium hydroxide, $NaOH$.

Most of the salts give ammonia as one of the products of decomposition, but some, as ammonium nitrite or nitrate give other products. (See nitrogen, §70, and nitrogen monoxide, §138.) The ammonium salts are easily made by neutralizing ammonium hydroxide with the appropriate acids.

391. Ammonium Chloride, NH_4Cl , commonly called sal ammoniac, is a white crystalline solid, obtained by neutralizing the ammonia liquor of the gas works with hydrochloric acid and evaporating the liquid to crystallization. It is purified by sublimation from stoneware pots and the crystals are condensed on a cold surface. It is easily soluble and has a sharp salty taste. It decomposes into ammonia and hydrochloric acid and may be made from a mixture of those gases. It is used in medi-

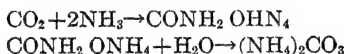
cine, in preparing ammonia gas or water, and large amounts are used for making batteries for open circuit work.

392. Ammonium Sulphide, $(\text{NH}_4)_2\text{S}$, is a colorless liquid of disagreeable odor made by saturating ammonium hydroxide with hydrogen sulphide and then adding an equal volume of ammonium hydroxide. If the second volume of ammonium hydroxide is not added to the saturated solution in making the sulphide, ammonium sulphhydrate, NH_4HS , is formed.



It becomes yellow on standing owing to decomposition whereby some sulphur is set free, which combines with the undecomposed ammonium sulphide forming polysulphides that contain from two to five atoms of sulphur, after which sulphur is deposited. The formula for ammonium polysulphide is written $(\text{NH}_4)_2\text{S}_x$. Ammonium sulphide and the polysulphide are used extensively in the laboratory for analytical work.

393. Ammonium Carbonate, $(\text{NH}_4)_2\text{CO}_3$. Dry ammonia gas and dry carbon dioxide give, when mixed, a white powder known as ammonium carbamate which gives the carbonate when mixed with water.



The ammonium carbonate of commerce is made by heating a mixture of equal parts of ammonium sulphate and chalk in a subliming apparatus which gives a sesquicarbonate that may be regarded as a mixture of ammonium carbonate, ammonium acid carbonate, and ammonium carbamate. It is a white powder undergoing decomposition in air. It is used in smelling salts, the small cubes of ammonium carbonate being moistened with ammonium hydroxide and perfumed with oil of lavender.

394. Ammonium Nitrate, NH_4NO_3 , made by neutralizing nitric acid with ammonia or ammonium hydroxide, consists of large transparent crystals soluble in water with a lowering of

temperature. At 300° it decomposes into nitrogen monoxide and water and its chief use is in the manufacture of nitrogen monoxide for medical and dental use. See §138.

395. Ammonium Sulphate, $(\text{NH}_4)_2\text{SO}_4$, is made by neutralizing dilute sulphuric acid with ammonia. When evaporated, colorless crystals are formed. They have a sharp taste and are soluble in two parts of cold or in one part of boiling water. It is largely used as a fertilizer and as a source of other ammonium compounds.

On September 21, 1921, the nitrate plant at Oppau, Germany, exploded, killing about 1500 people, injuring 3,000 more and producing physical effects that were felt at a distance of at least 35 miles, while a hole 100 feet deep and 400 feet in diameter was made where the plant had stood. The explosion apparently started in the laboratory where 2 gas tanks exploded. It is thought that the force of this explosion was transferred to the storage tanks that contained a mixture of ammonium nitrate and ammonium sulphate prepared to use as a fertilizer. Before the explosion occurred the color of the salt had changed from its usually pure white to a slightly yellow color and the temperature had risen from 100° to 120° F during the night preceding the explosion. The material tends to form a hard cake and it has been a custom to break the cake by blasting it with dynamite. During the past few years over 16,000 dynamite charges had been set off without serious results. Various tests had been made on the sensitiveness of this mixture when primed with dynamite but with negative results except when confined in an iron tube part of the mixture would explode. Fire and high temperatures do not seem to cause explosions. The capacity of the silos holding the mixture was 50,000 tons. How much exploded is unknown but the authorities admit that there were at least 4,500 tons in the silos at the time of the explosion. Two other lesser explosions have been reported since. Since the nitric acid used in producing the ammonium nitrate was made by synthetic processes and hence should have been free from

impurities, it is difficult to say just why these explosions occurred.

396. Problems.

1. Write quantitative equations showing the comparison of the Le Blanc and Solvay processes of making sodium carbonate (§371).
2. Write quantitative equations showing the production of sodium hydroxide by the electrolytic process. (§374).
3. How much potassium can be freed by the action of 50 grams of magnesium upon potassium hydroxide? (§381)
4. How much potassium iodide can be produced from 75 grams of potassium hydroxide according to the two equations given in §383?
5. How much potassium hydroxide can be made by the action of calcium hydroxide upon two tons of potassium carbonate? (§384).
6. How much potassium chloride will be required to produce 100 pounds of potassium chlorate according to the equations given in §386?
7. How much potassium cyanide can be produced from 500 pounds of potassium ferrocyanide? (§388)
8. How much potassium chlorate should be decomposed to yield two ounces of potassium chloride? (§35).

CHAPTER XVIII

CALCIUM, STRONTIUM AND BARIUM

The three metals known as the alkaline earth metals occur combined, and are hard to separate. Of the three calcium is by far the most abundant and important. Strontium and barium are often found together and in some localities are found with calcium.

397. Comparison of the metals of this chapter.

<i>Metal</i>	<i>At. Wgt.</i>	<i>Valence</i>	<i>Specific Gravity</i>	<i>Melts</i>
Ca	40 07	2	1 85	805°
Sr	87 63	2	2 50—2.58	900°
Ba	137 37	2	3 78	850°

CALCIUM

398. Occurrence. Calcium occurs as the carbonate, CaCO_3 , in limestone, marble, chalk, etc., as the sulphate, CaSO_4 , or gypsum; as the phosphate, $\text{Ca}_3(\text{PO}_4)_2$; and as the fluoride, CaF_2 . It is found as the carbonate and sulphate in water and as the phosphate in bones and phosphate rock. The compounds of calcium taken together form about 3.5% of the earth's crust.

399. Preparation. Until about the beginning of the present century calcium was a very expensive metal, in spite of its abundance, owing to the great difficulty of obtaining it from its compounds, a gram of the metal costing about \$10.00. Calcium is now obtained by electrolysis and the price has dropped to a much smaller figure, being about two to three times as expensive as aluminum. In obtaining metallic calcium by electrolysis fused calcium chloride is used in a graphite crucible, which forms the anode. The cathode is an iron rod which dips into the fused mass to some extent, but is gradually withdrawn so that

the calcium is always in contact with the fused salt. The calcium builds up on the cathode, its shape resembling a cabbage stalk.

400. Properties. Calcium is a whitish metal resembling aluminum. When pure it may be cut with a knife, but as produced commercially it is about 98% pure and in hardness stands between lead and brass so that it may be turned in a lathe and the shavings kept under petroleum. It may be used to decompose cold water, in which it sinks, but the evolution of hydrogen is far less violent than when sodium is used. Calcium will combine with many elements, the formation of the oxide, chloride, sulphide and phosphide being easily effected in a hard glass bulb-tube with the emission of light. Calcium tarnishes rather gradually in the air at ordinary temperatures, but when heated in a blast lamp it melts at 805° and if heated higher it burns with a brilliant flame forming the oxide and nitride. Burning calcium decomposes carbon dioxide, setting carbon free

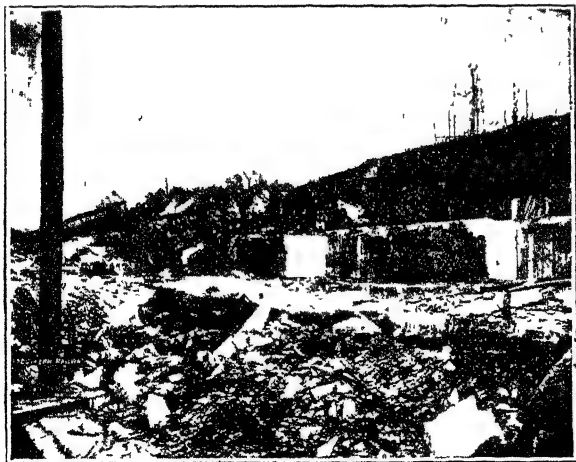


FIG. 108. A Marble Quarry.

COMPOUNDS OF CALCIUM

401. Calcium Carbonate, CaCO_3 , occurs in enormous quantities as limestone, marble, chalk, etc. (Fig. 108.) Iceland spar, which gives a double refraction of light, is a very pure calcium carbonate. Stalactites, which hang from the roof, and stalagmites, which rise from the floor of many caves, are formed by the depositing of calcium carbonate brought by water charged with carbon dioxide, the carbonate being deposited when the gas escapes (Fig. 109.) Chalk, formed from the remains of the

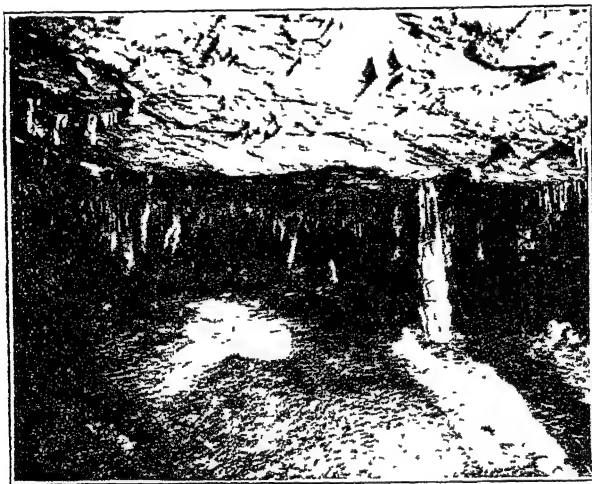


FIG 109 Stalactites and Stalagmites.

shells of minute sea animals, is another form of the carbonate and is very abundant in many parts of the ocean. When deposited in boilers the carbonate mixture is called boiler scale. (See Fig. 110.)

It is much easier to remove the scale-forming material before the water enters the boiler than it is to remove the scale after

it has formed. Many preparations are on the market for this purpose but one of the cheapest is a patented preparation called permutite.

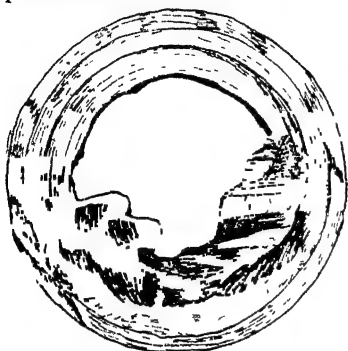


FIG. 110. Boiler Scale

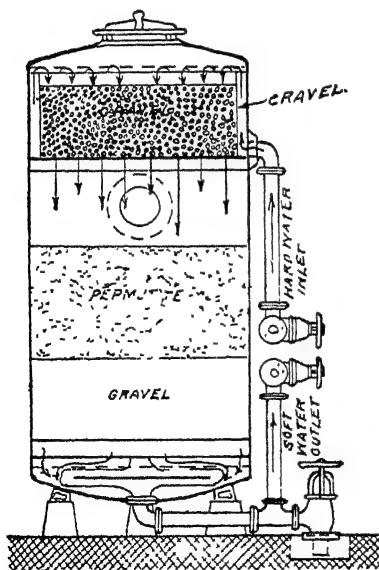
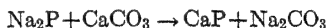


FIG. 111. Permutite.

Permutite is an artificial sodium silico aluminate. For convenience the formula is usually taken as Na_2P . The calcium salts producing hardness in the water react with the permutite, the calcium taking the place of sodium, making calcium permutite and after 12 hours the reaction is stopped and the tank is filled with a strong solution of sodium chloride and allowed to stand for 12 hours. (Fig. 111.) During the time the permutite is removing the calcium salts the reaction is expressed by the following equation



When the salt solution is added it reacts with the calcium permutite according to the following equation



Calcium chloride solution is drained off and the filter is again ready for use and since the salt is the only material consumed the original charges may last for several years.

It is claimed that zeolite or permutite does not furnish water of zero hardness; that the water will contain as much as 0.5 of a grain per gallon of hardness expressed in terms of CaCO_3 ; that there is increased tendency for foaming owing to the increased amount of sodium salts especially the carbonate which under the influence of steam pressure may break up and form acids that exert corrosive action.

It has been estimated that the railroads use 900,000,000,000 gallons of water annually, costing \$63,000,000 and that of this water only 21,600,000,000 gallons are chemically treated but that fully 350,000,000,000 gallons should be softened before being admitted to the boilers.

A report by the Great Northern Railway covering 1160 miles of track shows that they have 77 water purifying plants furnishing the water for the locomotive boilers. Hydrated lime and soda ash with ferrous sulphate are used as the coagulant. It has resulted in 30 to 40% increase in the tonnage hauled by each engine and a 50% reduction in boiler washing and the elimination of 11 failures.

The Missouri Pacific Railroad in 1918 with 52 plants treated 1,368,305,000 gallons of water. 3,509,473 pounds of boiler scale were removed. The cost of the investment was \$154,500. The cost of treatment was \$89,873 and the net saving was estimated at \$287,843.

Calcium carbonate is used in building, in road making, in the preparation of lime for mortar, in glass making, in the reduction of iron ore, etc. Chalk with clay is made into crayon; whiting is impure chalk, and putty is whiting mixed with 15 to 18% of linseed oil.

402. Calcium Oxide, CaO , known as quicklime, is made by burning limestone.

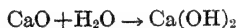
When pure limestone is heated the water in the stone is first driven off, and when the dissociation temperature is reached carbon dioxide is evolved according to the equation



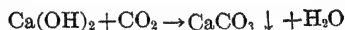
but often other substances, such as magnesium carbonate, iron oxide and aluminum oxide are found mixed with the limestone, and when the percentage of magnesium carbonate is 30 or more the rock is known as magnesian lime stone. When the rock is practically pure limestone 112 pounds of coal per ton is required to change the limestone into calcium oxide if the burning is continuous, and about 150 pounds if the burning is intermittent. Less coal is required if the percentage of calcium carbonate is lowered.

Calcium oxide is a white hard solid, nearly infusible. When heated in a hydrogen or an oxyhydrogen flame it gives an intense light, known as the lime, calcium or Drummond light. Exposed to the air it absorbs carbon dioxide and water, and is converted into the hydroxide and the carbonate, known as air slaked lime. Mixed with water it forms the hydroxide, $\text{Ca}(\text{OH})_2$, with high elevation of temperature. The process is known as slaking and the product is called slaked lime. (See below.) Calcium oxide is used as lime cartridges in coal mining, the mass swelling and exerting great pressure when wet with water. After converting it into calcium hydroxide (§403) it has many other uses.

403. Calcium Hydroxide, $\text{Ca}(\text{OH})_2$, formed by adding water to calcium oxide,

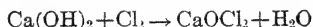


is a white powder somewhat soluble in water forming lime water. At red heat calcium hydroxide loses water and is converted to the oxide. If lime water is exposed to the air it absorbs carbon dioxide and forms a little calcium carbonate, which may exist as a crust on the surface of the water, or if the carbon dioxide is conducted into the lime water, the carbonate causes cloudiness.



This forms a good test for the presence of carbon dioxide. If the hydroxide is present in abundance in suspended particles the solution is called milk of lime. This is used for white-

washing. Mortar is formed by slaking calcium oxide with water, adding sand and hair. It hardens without much shrinking and lasts a long time unless exposed to the action of the weather, which causes it to crumble slowly. Mortar gradually absorbs carbon dioxide from the air forming calcium carbonate as in the preceding equation. If layers of calcium hydroxide are exposed to the action of chlorine, bleaching powder, CaOCl_2 , is formed.



When the powder is mixed with sulphuric or hydrochloric acid, the chlorine is set free. Enormous quantities of bleaching powder are used for bleaching, as a disinfectant, etc., since it is an easy way to transport and to obtain chlorine. It is often called chloride of lime.

Bleaching powder for use in hot countries may be stabilized by adding 20% of calcium oxide, or by the addition of sodium chloride.

404. Calcium Sulphate, CaSO_4 , occurs in nature in volcanic regions as gypsum, containing two molecules of water of crystallization, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. One part of gypsum is soluble in 500 parts of water at 18° .

Gypsum is 79.1% calcium sulphate. When heated to 100° C. or more, water is given off, but the heating must not exceed 205° and usually ranges from 170° to 200° when $\frac{3}{4}$ of the water is given off forming plaster of Paris $(\text{CaSO}_4)_2 \cdot \text{H}_2\text{O}$. This is 93.8% CaSO_4 and when mixed with water, the water is again combined as water of crystallization, and the mass becomes hard in a short time. Complete dehydration of pure gypsum gives flooring plaster, and if mixed with alum, borax, etc., gives a hard finish plaster. One formula for flooring plaster is dehydrated gypsum with 0.4% calcined sodium sulphate or potassium sulphate, and this is mixed with sand or ashes. Such substances as glue, sawdust, blood, tankage of packing houses, etc., act as retarders when mixed with plaster of Paris, the usual proportions being from 2 to 15 pounds of the retarder per ton

of plaster. Dental plaster is plaster of Paris to which an accelerator, such as common salt, has been added.

405. Hydraulic Limes or Cements may be defined as cementing materials made by burning siliceous or argillaceous limestones, whose clinker, after calcination contains so large a proportion of lime silicates as to give hydraulic properties but also so much free calcium oxide that the mass of the clinker will slake when water is added, but not enough to prevent hardening under water. (Fig. 112.) Ideal hydraulic lime is said to contain

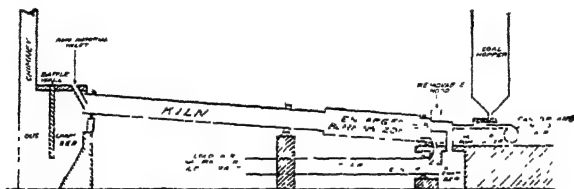


FIG 112. Cement Kiln

before slaking 21.2% SiO_2 ; 78.8% CaO ; and no water or carbon dioxide. After slaking it should contain 19.08% SiO_2 ; 70.92% CaO ; 10% water and no carbon dioxide; but actual conditions usually show a lower lime content with impurities such as Al_2O_3 and Fe_2O_3 .

So-called Natural Cements vary widely in composition and are produced by burning a natural clayey limestone containing from 15 to 40% SiO_2 , Al_2O_3 and Fe_2O_3 , without preliminary mixing and grinding. After burning without grinding the mass will not slake when water is poured upon it, but after grinding the powder will set under water. The use of natural cements is usually limited to the area near where they are found. (Fig. 113.) They set rapidly, but are not as strong as Portland cement.

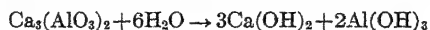
Portland cements have a very definite composition and are made by pulverizing the clinker produced by burning to semi-fusion an intimate mixture of calcareous or argillaceous materials

containing approximately 3 parts of CaCO_3 to 1 part of SiO_2 , Al_2O_3 and Fe_2O_3 . The ratio of the lime in the finished product should not be less than 1.6 to 1 or more than 2.3 to 1. The composition approaches the formula $3\text{CaO}.\text{SiO}_2$, tricalcic silicate corresponding to 73.6% CaO , and 26.4% SiO_2 . The composition varies somewhat, and impurities or added ingredients may change the composition still further.



FIG. 113. Natural Cement Beds in Indiana.

Portland cements become as hard as stone when mixed with sufficient water to set the cement, forming a network of aluminum silicate, calcium silicate and calcium metaluminate. The silicates form a filler and the aluminate is hydrolized.



Slag cement is an intimate mechanical mixture of slaked lime and granulated blast furnace slag all finely pulverized.

The slag must be obtained from a basic blast furnace and must analyze SiO_2 and Al_2O_3 not over 49%; O, 10 to 16%; MgO not less than 4%. It must be made in a hot furnace and be light gray in color. The slag is thoroughly disintegrated by the action of a large stream of cold water directed with considerable force against the hot slag. The action of the cold water upon the hot slag makes it energetically hydraulic and removes a portion of the sulphides. The slag containing 15 to 40% water is then dried at a dull red heat so as not to disintegrate it, and is mixed with carefully slaked, finely ground lime in the proportion of 20 to 40 parts of lime to 100 parts of slag.

Comparison of Slag and Portland Cements. Slag cement sets very slowly as compared with Portland. It costs considerably less than Portland to manufacture. Its specific gravity varies from 2.7 to 2.9 as against 3.15 for Portland.

Experiments carried out in the North Sea for a period of three years indicate that concrete containing blast furnace slag protects the embedded reinforcing material perfectly, and is from 5% to 9% stronger than cements and concretes not containing iron slag.

Slag bricks are made by mixing granulated slag with slaked lime or with slag cement, molding the mixture in a brick press, and drying either with or without the aid of steam. Slag blocks, slag tile, etc., are made in the same manner.

406. Concrete consists of a mixture of cement and loose stony material such as sand, gravel, crushed limestone or cinders with water. It is not as strong as cement, but is much less expensive. The usual proportions call for 1 part of cement with 3 or 4 parts of rock material, but varies either way, a larger proportion of rock cheapening the product while a larger proportion of cement makes it stronger. (Fig. 114.) About six months are required for a concrete to acquire full strength in setting, after which it falls off slightly, but when it is at its maximum strength a good concrete will withstand a pressure of 5000 to 7000 pounds per square inch without being crushed.

Reinforced Concrete is produced by embedding twisted steel rods in the concrete. This may be done by building a steel framework of the rods and constructing around it a wooden mold, into which the concrete is poured. The molds are not removed until the concrete has hardened.

Cinder Concrete substitutes coal cinders for the stone of ordinary reinforced concrete. It is suitable, for constructing floor fillings in fire-proof buildings since it is the only kind of concrete that can withstand without crumbling the sudden changes of temperature when water is poured upon a burning building.

407. Calcium Chloride, CaCl_2 is found in nature in combination with other chlorides as magnesium chloride; and exists in sea water. It may be made in several ways, one being the action of hydrochloric acid on calcium carbonate. From very concentrated solutions calcium chloride forms crystals containing six molecules of water of crystallization which deliquesce in the air. If the solution is evaporated at a temperature lower than 200° , the crystals contain only two molecules of water and form a porous mass which loses its water when heated above 200° , becoming fused calcium chloride, often used as a drying agent because it absorbs water readily. Mixed with snow a temperature of -40° is produced. A 40% solution of calcium chloride is sometimes used as an anti-freeze mixture for auto radiators, but since it corrodes copper and aluminum it is not considered

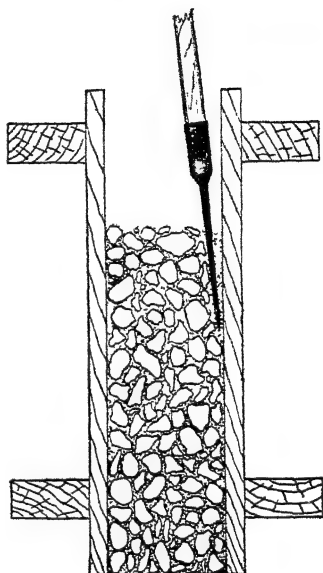


FIG 114 Building a Concrete Foundation.

satisfactory if it comes in contact with these metals. A 3% solution is used as an anti-freeze compound in mixing cement and concrete.

408. Calcium Fluoride, CaF_2 , or fluorspar, occurs in crystallized cubes and is the source of the fluorine compounds. (§214.) It is used as a flux in certain reactions that occur at high temperatures, the flux taking the place of water at low temperatures.

STRONTIUM AND BARIUM

409. Strontium and barium are rare metals resembling calcium in both physical and chemical properties. They always occur combined and are never used, although a few of their compounds are used to some extent.

410. Strontium Compounds. Strontium oxide, SrO , and strontium hydroxide, $\text{Sr}(\text{OH})_2$, are made in the same way as the analogous calcium compounds. The hydroxide is used to some extent in the manufacture of beet sugar. **Strontium nitrate** $\text{Sr}(\text{NO}_3)_2$, is used for red fire when mixed with potassium chlorate and shellac.

411. Barium Compounds. Barium chloride, BaCl_2 , is used as a test for sulphuric acid since it forms insoluble barium sulphate, when sulphuric acid or a soluble sulphate is added. **Barium oxide**, BaO , and **barium dioxide**, BaO_2 , were formerly used in the extraction of oxygen from the air. **Barium hydroxide**, $\text{Ba}(\text{OH})_2$, forms baryta water when dissolved, reacting in the same way as lime water when carbon dioxide is introduced. It is more soluble than the calcium hydroxide. It is used extensively in the analysis of iron and steel for the estimation of carbon as carbon dioxide. **Barium sulphate**, BaSO_4 , is prepared as a pigment known as permanent white. It occurs in nature as heavy spar. It is used to increase the weight of paper and to give it a gloss. **Barium nitrate** is used for making green fire when mixed with potassium chlorate and shellac. It is also an

important ingredient in "sparklers" two formulas being in parts by weight:

	$Ba(NO_3)_2$	$Fe(filings)$	$Al(filings)$	<i>dextrin</i>
No. 1	25	15	4	6
No. 2	18	20	2	$1\frac{1}{2}$

The ingredients are reduced to a very fine powder, made into a paste with water and when entirely free from lumps the paste is applied to wires.

The addition of a small amount of potassium chlorate and powdered magnesium makes them more brilliant.

Barium sulphide, BaS , **strontium sulphide**, SrS , and **calcium sulphide**, CaS , shine feebly in the dark after being exposed to the direct light of the sun, and are used in luminous paints. A highly phosphorescent calcium sulphide is made by heating precipitated chalk with 30% of its weight of powdered roll sulphur in a closed crucible for an hour. After cooling the product is impregnated with 0.0001% of bismuth in the form of an alcoholic solution of bismuth basic nitrate. The mass is then heated again to a dull red heat for two hours and is allowed to cool in the closed furnace.

Neither strontium nor barium salts are used where the corresponding calcium salt may be used because the calcium salt is cheaper and owing to the lower atomic weight of calcium, the calcium salt will contain a higher percentage of the acid radical. This is similar to the use of sodium and potassium salts. (§362.)

412. Problems.

1. How much calcium carbonate must be used to produce 25 kilograms of calcium hydroxide? (§§402, 403)
2. How much calcium carbonate must be used to produce 10 liters of carbon dioxide? (§402 or §262).
3. How much hydrochloric acid will react with a cube of marble three centimeters on a side if the specific gravity of marble is 2.72? (§262).

CHAPTER XIX

IRON, NICKEL AND COBALT

These three metals have atomic weights very nearly the same, but the atomic weight of iron is more nearly the same as that of manganese which it resembles in many ways. Nickel and cobalt are closely associated and are found together in nature. The properties of the three metals are very similar.

413. Comparison of the metals of this chapter.

<i>Metal</i>	<i>At. Wgt.</i>	<i>Valence</i>	<i>Specific Gravity</i>	<i>Melts</i>
Fe	55 84	2,3	7 85—7 88	1100—1700°
Ni	58 68	2,3	8 6 —8 9	1452°
Co	58 97	2,3	8 4	1478°

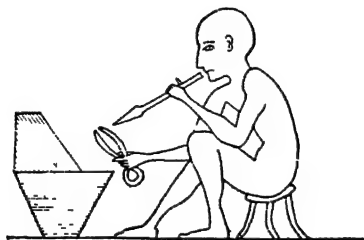


FIG 115. Early Egyptian Blast Furnace

IRON AND STEEL

414. Occurrence. Iron is the most generally useful of all the metals. It has been known for many hundreds of years but as its preparation and working are difficult, it was not the first metal used by man, as the bronze age preceded the iron age. Probably the first iron was derived from meteorites, which are

usually mixtures of iron and stone in varying proportions, some of which contain one substance very nearly to the entire exclusion of the other. Free iron is very rare but in compounds iron is both abundant and widely distributed, the chief source of the metal being the ores hematite, Fe_2O_3 , which occurs in abundance south of Lake Superior in Michigan, in Alabama and Tennessee; limonite, or brown hematite, $\text{Fe}_2\text{O}_3 \cdot \text{Fe}_2(\text{OH})_6$, in Alabama, Tennessee, Virginia and West Virginia; magnetite, Fe_3O_4 , in Pennsylvania, New Jersey and New York; and siderite, or spathic iron ore, FeCO_3 , in Ohio, Maryland and New York. Less than 1% of the iron made in the United States is obtained from siderite.

It has been predicted that the present known reserve of high grade iron ore in this country will be exhausted in 20 years. The electric smelting is said to make possible the use of iron sands and low grade ores that are now considered worthless

The relative percentages of iron ore in European countries is now given as France 35.7%, Great Britain 18.2, Sweden 12.5, Germany 11.1, Spain 5. Central Russia 4.2, Norway 3.3 and the remaining 10% is in 15 different countries. In 1914 the distribution gave Germany 26.5, France 20.4, Great Britain 15, Spain 9.1. If the ore of all Europe is estimated as 1 the ore in North America is 3, South America 2, Asia 0.75, and Africa 0.166 from known deposits.

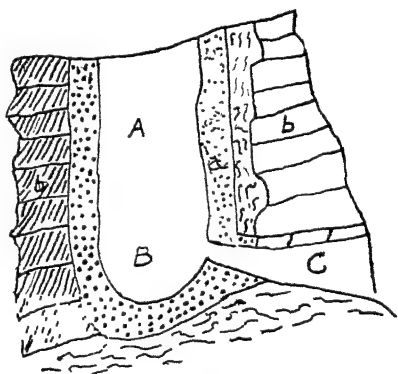


FIG 116. Prehistoric Iron Furnace

The most abundant iron compound that is not used as a source of iron, is iron disulphide, FeS_2 , or pyrites, often called

Fools' Gold because of its weight and yellow color. Iron is also contained in pyrrhotite, which varies in composition from Fe_9S_7 to $\text{Fe}_{11}\text{S}_{12}$; in the double sulphides of iron and copper

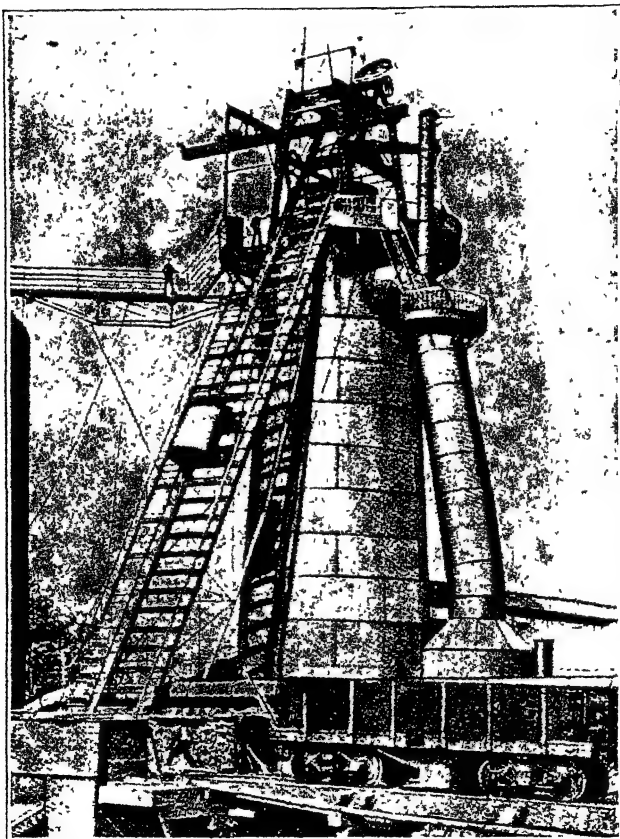


FIG. 117. A Modern Blast Furnace.

known as chalcopyrite, CuFeS_2 , and bornite, Cu_5FeS_4 , and in the double sulphide of iron and arsenic, FeSAs . The ores are usually

mixed with more or less clay, silica, etc., and contain small amounts of phosphorus, sulphur and manganese with occasionally other substances.

415. Preparation. Pure iron is almost unknown. Crude iron is prepared by heating the ore together with lime-stone and coke in a blast furnace. (Fig. 117.) The furnace is from 90 to 105 feet high and the inner diameter is from 12 to 16 feet. After the substances are mixed they are carried to the top of the furnace by a mechanical hoist where the mixture enters through a double hopper, the escape of the gases and heat being prevented by two bell-shaped valves which open one at a time when the ore presses upon them. After the fire has been started in the furnace and the ore mixture is added, compressed air previously dried and heated to a temperature of 400° to 600° having a pressure of 12 to 15 pounds per square inch is blown in. This burns the coke producing an intense heat that melts the charge. From 3 to 4 tons of air are required for every ton of iron produced. The gases formed usually contain about 20% by volume of carbon monoxide and have half the heating capacity of coke. At the top of the furnace they have a temperature of 200° to 400° and are in part conducted to the stoves, which heat the air before it is blown into the blast furnace, through the tuyeres (pronounced tweers) which are large hollow pipes entering near the bottom of the furnace. (Fig. 118.) The rest of the gas is utilized in various parts of the plant for heating purposes, partly to generate the steam that supplies the power to the engines that compress the air, before it enters the furnace. (See §816).

The coke which is sometimes mixed with coal, is used for fuel to keep up the high temperature. The limestone is added as a flux, or, if the ore contains lime, feldspar and sand are used. The flux removes the impurities in the form of a fusible slag or cinder and further, prevents the reduced iron from reuniting with the oxygen that is being blown in. As the smelting continues, the iron falls through the slag to the bottom of the

furnace below the tuyeres into what is known as the crucible. Fresh charges are added from time to time and the operation is continuous through months or even years.

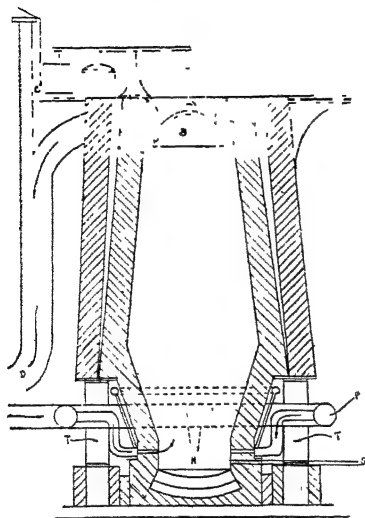


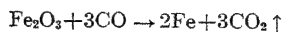
FIG. 118. Cross Section of a Blast Furnace.

About every two hours the slag is tapped through the cinder notch, and about every four or six hours the metal is drawn off through the metal tap. The cinder notch is closed by a plate which chills the slag around it, thus closing the opening. The metal tap is closed with clay which is forced in by a steam ram, and becomes so hard that it often has to be drilled out. (Fig. 119.)

A large furnace will produce about 500 tons of iron per day. The iron always contains impurities, a small amount of phosphorus, three or four per cent of carbon,

some sulphur, and about three per cent each of manganese and silicon. The impurities cause the iron to melt at a temperature of about 1200° instead of 1800° or more.

416. The Chemical Changes that reduce the iron ore in the furnace are simple. First the fuel is changed to carbon dioxide by the air. The carbon dioxide is changed to carbon monoxide as it passes up over the hot coke, and the carbon monoxide unites with the oxygen of the ore to form carbon dioxide while metallic iron is set free. The main reaction may be expressed by the equation



but some of the Fe_2O_3 probably forms FeO and is reduced by the carbon in the lower part of the furnace.

After the iron comes from the blast furnace it is either sold as iron or is changed into steel. When used as iron it may be divided into two general classes—cast iron and wrought iron.

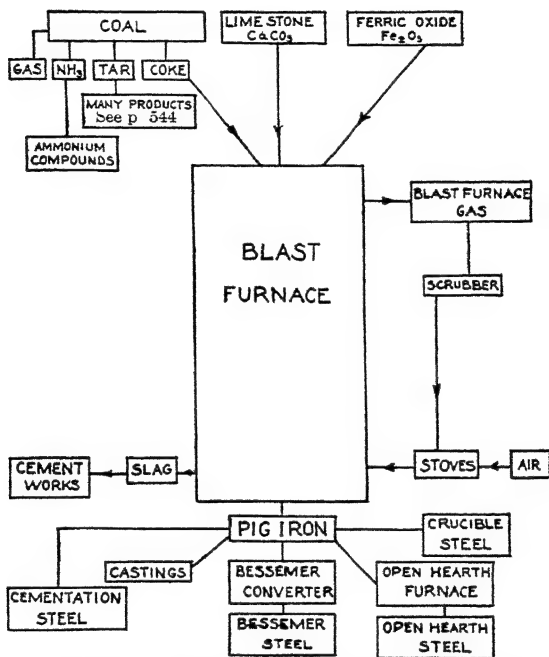


FIG. 119. Outline of the Blast Furnace Process

CAST IRON, WROUGHT IRON AND STEEL

417. Cast Iron is the most impure and is brittle and white or gray in color, according to the distribution of the carbon it contains. If the iron is cooled rapidly, the carbon is combined with the iron, and it is known as white cast iron. If the iron is cooled slowly, the carbon is uncombined, remains as graphite,

and the iron is called gray cast iron. Cast iron is known also as pig iron. On account of its brittleness it is not welded or forged but is cast in molds to the desired shape. It may, however, be welded by converting the brittle surfaces into ductile metal by the electric arc and the welding metal will then adhere. It is strong and is used extensively in all iron foundries. It is easily fusible, the gray iron fusing at a lower temperature than the white.

Wrought Iron is the purest commercial iron and is made from cast iron by a process known as puddling, by which the carbon, silicon, manganese, phosphorus and sulphur are burned out of the cast iron in a reverberatory furnace lined with hematite or magnetite. The oxygen necessary for the oxidation of these substances is furnished partly by air, partly by the oxides of iron that form the linings of the furnace. The metal becomes less fusible and turns to a pasty mass containing some slag that cannot be removed. The iron is then gathered into large masses and is hammered or rolled. The impurities are mostly the slag which permits easy welding and prevents the tendency to crystallize, due to the small amounts of phosphorus and sulphur

still present. The impurities other than the slag usually amount to less than 1%.

Steel, which with respect to the amount of carbon it contains, stands midway between cast iron and wrought iron is made in several ways, the problem being to get the proper amount of carbon. The fastest and cheapest method is the Bessemer process.

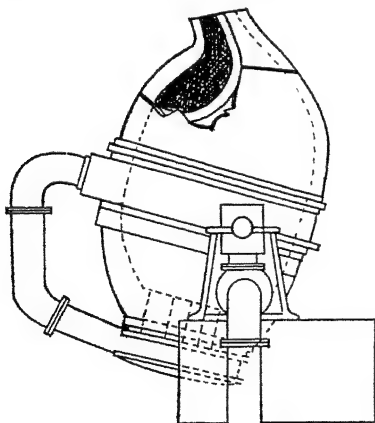


FIG. 120. A Bessemer Converter.

In this process the pig iron is oxidized in a converter, which is a large vessel shaped somewhat like an egg, so supported that it may be turned about its axle, called its "trunnions," by means of compressed air. At the bottom of the converter is the wind box which receives the compressed air from a pipe leading from one of the trunnions, and delivers it through openings, called tuyeres, through the bottom of the converter. The converter is rotated to a horizontal position, about 10 tons or more of molten pig iron from the blast furnace is run in, the blast of 20 to 30 pounds per square inch is turned on and the converter is rotated

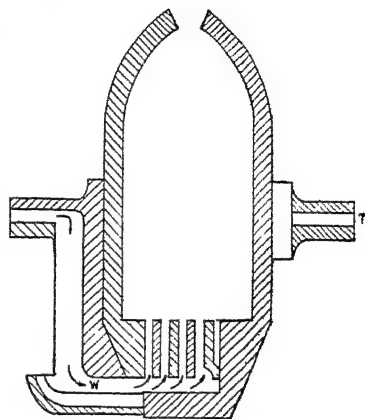


FIG 121. Cross Section of a Bessemer Converter.

until it is nearly vertical. The air is forced through the mass for about 15 minutes, the exact time being determined by the nature of the flame that issues from the mouth of the converter. (Fig. 122.) The temperature is kept down to such an extent that the other impurities are burned to oxides before the carbon oxidizes. Pieces of pig iron are frequently added to accomplish this. Toward the end of the process the temperature is increased, the carbon is oxidized to carbon monoxide and burns with a bluish flame at the mouth of the converter. As soon as the carbon is all burned out, the flame drops and the converter is turned down before the blast is completely turned off. The sulphur and phosphorus are not removed by the air blast, but if they are present in large quantity they may be removed by lining the converter with basic material, such as magnesium and calcium carbonates. This is known as the Thomas-Gilchrist process, and the slag, known as Thomas slag, contains phos-

phorus, making it valuable for fertilizers. Hot lumps of ferromanganese or spiegeleisen are added to supply the necessary carbon and manganese. The metal is then poured into a large

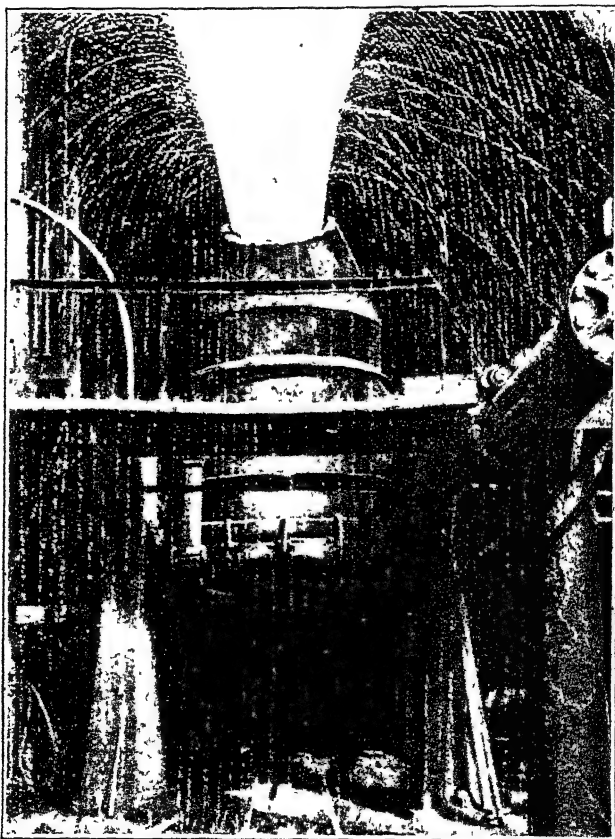


FIG. 122. A Bessemer Converter in Action.

ladle and is poured from this into molds holding about two tons each, which are cooled and then reheated to secure a uniform

temperature, and rolled into the desired shape by passing the metal back and forth between rapidly revolving rollers which are gradually brought closer and closer together until the final form and size are obtained, after which the metal is sent to the finishing room to be straightened, etc.

The spiegeleisen or spiegel iron contains 4 or 5% of carbon and 5 to 20% of manganese. Ferromanganese contains 6 or 7% of carbon and 25 to 85% of manganese. If much spiegel is added a hard or high carbon steel is produced while a small amount of the ferromanganese gives a soft or low carbon steel which has practically replaced wrought iron.

OTHER METHODS OF MAKING STEEL

418. In the Open Hearth Process, known as the Siemens-Martin process, pig iron, scrap iron or steel, and iron ore are melted in a reverberatory furnace heated by the regenerative principle, by which the waste gases from the furnace heat two compartments filled with fire bricks until very hot. (Fig. 123.) Furnace gas is now shut off and fuel gas is passed through one compartment, air through the other, thus producing an intense heat at the top of the furnace. While these two compartments are being cooled by the passage of the gas and air through them, two similar compart-

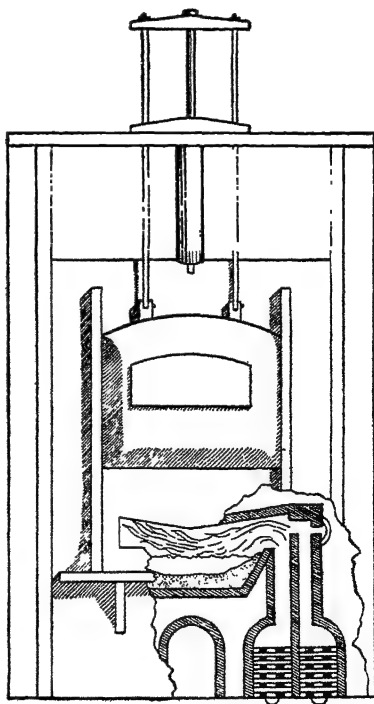


FIG. 123. An Open Hearth Furnace.

ments are being heated on the other side of the furnace and as one set becomes cool the gas and air are turned into the other two, the alternation which occurs every 20 minutes or so making it possible to keep the high temperature necessary to oxidize the impurities.

The open hearth process requires from 6 to 12 hours as compared with about 20 minutes by the Bessemer process, and taking the extra fuel into account is more expensive. However, iron with any percentage of phosphorus may be used, while in the Bessemer process about 2% of phosphorus is required for the best results. The steel made by the open hearth process is of excellent quality, being tough and elastic. It is used for the steel beams of large bridges, for large guns, large machines, and in nickel steel which is used for armor plate.

In the Crucible Process, 80 pounds or less of wrought iron is mixed with the proper amount of carbon in the form of charcoal and heated for three or four hours in clay or graphite crucibles. Manganese oxide is sometimes added to make the metal better adapted for forging. Crucible steel as used for razors contains 1.5% carbon; if used for tools it contains 1%; and 0.75% for dies, pens, needles, etc.

Electric steel is now being produced in ever increasing quantities. The heat is produced by the electric current, both the induction and electrode type of furnace being used, but the latter is practically more satisfactory. The temperature produced is far in excess of that produced in the crucible or open hearth furnaces. Most of the furnaces are small, holding $1\frac{1}{2}$, 3 or 5 tons and requiring $1\frac{1}{2}$ to 2 hours to melt the charge, but in France furnaces holding 25 tons of cold or 30 tons of liquid iron are common, while some run as high as 60 tons. (Fig. 124.)

In making crucible steel the charge must be of high and analyzed grade and the sulphur, manganese and phosphorus cannot be removed owing to the lack of oxidizing and basic materials. In the electric furnace the sulphur and phosphorus may be reduced to 0.02% or less due to the oxidizing and reduc-

ing conditions of the slag which in turn are obtained with the electric furnace. A slag consisting of about 60% of silicon dioxide, 15% of calcium oxide, 15% of calcium fluoride and 10% of carbon is extremely fluid and enables the charge to be freely manipulated. Silicon and manganese additions are made in the furnaces and aluminum is added in the ladle to finish deoxidizing. Loss of iron and added alloys is thus reduced.

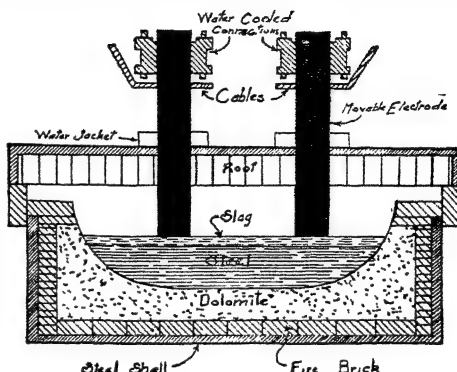


FIG. 124. An Electric Furnace for Steel

The electric furnace will do all that can be done with the basic open hearth furnace and while some claim that crucible steel is best for fine tools others say that electric steel is fully as satisfactory.

The increase in the production of electrical steel from 1913 to 1918 was 1700% in the United States, 600% in Germany, 700% in Great Britain, 2100% in Canada. The output in 1918 was 511,364 tons in the United States; 221,824 tons in Germany; 147,922 tons in Great Britain; 120,000 tons in Canada; 58,000 tons in France, with some amounts in Austria, Hungary, Italy and Sweden, bringing a total of 1,155,173 tons.

419. Comparison of Cast Iron, Steel and Wrought Iron.

<i>Kind</i>	<i>Melts about</i>	<i>Average per cent of C.</i>	<i>Impurities per cent</i>	<i>Malleability</i>	<i>Grain</i>	<i>Temper</i>
Cast iron	1100°	1.5 to 6	5 to 10	brittle	coarse	none
Steel	1400°	0.7 to 2	1 to 2	somewhat malleable	fine	good
Wrought iron	1700°	0.15	0.36 to 0.5	very malleable	very fine	none

420. Properties of Iron. Wrought iron is the purest that may be obtained and is used for piano strings containing only 0.3% of impurities. Pure iron may be made by igniting the oxide or oxalate in a current of hydrogen, by reducing the chloride by hydrogen, or by electrolytic methods. When perfectly pure it is white, is softer than the ordinary iron and melts at a higher temperature. Its specific gravity is about 7.85. Dry air or water freed from air does not rust iron, but moisture, air and carbon dioxide combined, produce a complex hydroxide having a formula of $\text{Fe}_2\text{O}_3 \cdot \text{Fe}_2(\text{OH})_6$, and after the surface starts to rust the change spreads rapidly. The rust and the iron seem to form a voltaic cell and decompose the water present, the hydrogen of which unites in part with some of the nitrogen of the air to form ammonia. Soft iron is magnetic and may be made a temporary magnet, but it soon loses its magnetism. Iron decomposes water at red heat. It reacts with hydrochloric or sulphuric acid, giving the salt of the metal and ill smelling hydrogen. This is caused by the impurities in the iron, such as the sulphide, phosphide and carbide, producing hydrogen sulphide, phosphine etc., which are evolved with the hydrogen.

With moderately dilute nitric acid, red vapors of nitrogen tetroxide are evolved. The concentrated acid covers the surface with a gas which protects it from further action, so that the dilute acid will not then act on the iron unless it is touched with such an object as a copper wire.

421. Properties of Steel. Steel takes a high polish, is ductile and malleable when hot, and melts at a temperature at which wrought iron becomes soft. Steel may be tempered or made hard, by being heated and then suddenly cooled by plunging it into cold water or oil. If heated and cooled slowly it becomes soft, tough, and elastic. The hardness of the steel will vary with the difference in the temperatures of heating and cooling and the rapidity of the cooling. When steel is rapidly cooled in the air for 6 to 8 minutes instead of 30, by use of an air blast of about 10 ounces pressure, the strength is increased from

about 4,000 to 10,000 pounds. Steel is hard to magnetize, but when once magnetized it will retain its magnetism for a long time. The addition of cobalt, tungsten, molybdenum, chromium or vanadium improves the steel for making permanent magnets. Low carbon steel can be forged, rolled or hardened. The effect of the phosphorus present as an impurity in steel is to make the steel brittle when cold, while the sulphur makes it brittle when hot. Other substances added to steel cause it to acquire certain desired properties.

When *aluminum* is added to open hearth steel better ingots free from blow holes are produced. If 10 to 15% of *titanium* is added to open hearth steel it combines with both nitrogen and oxygen and passes into the slag. The resulting steel is about 40% more durable than the ordinary open hearth steel. Other substances are often added, forming

STEEL ALLOYS

<i>Alloy</i>	<i>Steel</i>	<i>Other Constituents</i>	<i>Uses, etc.</i>
Manganese steel	80 to 93	Mn, 7 to 20	Holds temper when heated. Used for rock crushing machinery and burglar-proof safes.
Tungsten steel	70 to 90	W, 8 to 20 Cr, 3 to 8	Holds temper when heated red hot by friction. Used for high speed tools.
Chromium-vanadium steel	99	Cr, 1 V, 0.15	Great tensile strength. May be bent double when cold. Used for axles, connecting rods, etc.
Nickel steel	96 to 98	Ni, 2 to 4	Great elasticity and hardness. Resists corrosion. Used for armor plate on battle ships.
Invar	64	Ni, 36	Nearly non-expansive. Used for pendulum rods, meter sticks, etc.

Stainless Steel. So-called stainless steel which resists rust contains carbon 0.2–0.4%, chromium 11.4–14%, manganese

not over 0.5%, silicon not over 0.3%. The phosphate and sulphur are kept as low as possible. The hardness of the steel is directly proportional to the carbon content. If it contains less than 0.25% carbon it will not harden successfully. If it contains more than 0.4% it is difficult to forge. The presence of silicon neutralizes the hardening effect of the carbon and gives a cleaner, sounder metal. The presence of phosphate and sulphur aids corrosion.

Before 1908 very little alloy steel was produced, but at present the annual output is over 2,000,000 tons. Chromium, molybdenum and tungsten impart to the steel properties that are closely analogous, and it is assumed that vanadium will do the same. Silicon, aluminum, titanium and zirconium act as deoxidizers within certain limits. The special elements added to act upon the carbon probably tend to keep the carbon in solution, or to aid in throwing it out of solution as a single or complex carbide, or to keep it in solution to a certain extent and to throw the rest out as carbides. In 1864 only 13,627 tons of steel were produced in the United States. Now the production annually is almost 45,000,000 tons.

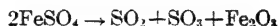
422. Compounds of Iron. Two series of iron compounds occur. Ferrous compounds are those where the iron acts as a bivalent and the ferric compounds are those where the iron is trivalent. The color of the ferrous salts is pale green, while the color of ferric salts is usually yellow to red brown.

The ferrous compounds may be changed to the ferric by the addition of an acid. The ferric change to ferrous when a reducing agent such as hydrogen, hydrogen sulphide or sulphur dioxide is added.

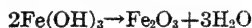
For this reason, ferrous, and not ferric, salts are produced when iron acts upon dilute sulphuric or hydrochloric acid, since the ionic hydrogen acts as a reducing agent.

423. Oxides. There are three oxides of iron. *Ferrous oxide*, FeO , is an unstable black powder formed by heating ferric oxide in a current of gas, composed of equal volumes of carbon mon-

oxide and carbon dioxide. *Ferric oxide*, Fe_2O_3 , occurs native as hematite. It may be prepared by calcining ferrous sulphate, which first loses water and then decomposes, two molecules of the sulphate giving one each of sulphur dioxide, sulphur trioxide and ferric oxide.



or by heating ferric hydroxide.



It is used in red paint, in jewelers' rouge, and is known by several names as crocus, Venetian red, etc. *Ferrous-ferric oxide* Fe_3O_4 , occurs as magnetite which may or may not be magnetic. It forms on the surface of iron as black scales when iron is heated to redness in air. It may be regarded as a compound of the other two.

424. Hydroxides. *Ferrous hydroxide*, $\text{Fe}(\text{OH})_2$, is a white precipitate formed when an alkaline hydroxide is added to a ferrous salt solution. It gradually oxidizes to the ferric hydroxide, turning brown. *Ferric hydroxide*, $\text{Fe}(\text{OH})_3$, formed by adding ammonia to a solution of a ferric salt, is a brownish red powder. When filtered, washed and dried it remains unchanged, but changes when heated to 100° or when boiled.

425. Chlorides. *Ferrous chloride*, FeCl_2 , is obtained when dry hydrochloric acid gas acts upon metallic iron, forming white pearly scales. If a solution of hydrochloric acid is used, the salt obtained by evaporation is green, containing four molecules of water of crystallization. *Ferric chloride*, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, containing about 21% of iron formed by passing chlorine gas over iron filings in a porcelain or glass tube, or by passing chlorine into a solution of ferrous chloride, may be obtained as yellow crystals containing six or twelve molecules of water. The anhydrous chloride is black. It has an acid reaction due to hydrolysis. A solution containing 29% of anhydrous ferric chloride contains 10% of iron. The tincture was formerly used

in diphtheria usually diluted with an equal volume of water. It is styptic in its action and has an acid and disagreeable taste, often producing nausea.

426. Sulphates. *Ferrous sulphate*, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, called green vitriol or copperas, is formed when dilute sulphuric acid acts upon iron, or by oxidizing iron pyrites, FeS_2 , by roasting or exposing the pyrites to air. Ferrous sulphate effloresces, and if exposed to moist air oxidizes. When heated to 114° it loses six molecules of water of crystallization, and the seventh at 300° . At 10° , 100 parts of the sulphate will dissolve in 164 parts of water while at 100° only 30 parts of water are required. It is used for making ink, as a disinfectant, in tanning, dyeing, making iron salts, in the reduction of indigo, in photography, etc.

Ferric sulphate, $\text{Fe}_2(\text{SO}_4)_3$, may be formed by oxidizing ferrous sulphate with nitric acid. It unites with potassium sulphate or ammonium sulphate to form iron alums. In color, ferric sulphate is greenish white, dissolving slowly in water to a yellow brown solution having an acid reaction.

427. Ferrous Carbonate, FeCO_3 , exists in clay. The action of water and carbon dioxide changes it to the bicarbonate, having the formula $\text{Fe}(\text{HCO}_3)_2$, and it is found in all well and river waters. When exposed to the air it oxidizes and rust is deposited. This will appear on glasses and other vessels where it produces an unsightly appearance. It may be removed from bottles in which iron salts have been standing in solution, or from other glassware by adding a mixture of concentrated nitric and sulphuric acids.

428. Sulphides. *Ferrous sulphide*, FeS , may be made by fusing fine iron filings with sulphur, or by the action of ammonium sulphide on a solution of a ferrous or ferric salt. It is usually brownish black, brittle and metallic looking when made by dry methods, but is yellow when pure. It is used for making hydrogen sulphide. *Ferric sulphide*, FeS_2 , occurs as pyrites and is common. It has a metallic brassy look, often mistaken for gold. It is not reduced for iron, but is used to obtain

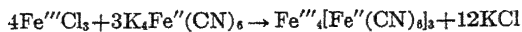
sulphur used in making sulphuric acid, in which enormous quantities are used. Other sulphides of iron vary in composition from Fe_8S_7 to $\text{Fe}_{11}\text{S}_{12}$.

429. Cyanides. Iron and potassium form two important cyanides, potassium ferrocyanide, $\text{K}_4\text{Fe}(\text{CN})_6$, and potassium ferricyanide, $\text{K}_3\text{Fe}(\text{CN})_6$, corresponding to the other ferrous and ferric compounds, the latter having the larger proportion of iron for each atom of potassium.

Potassium ferrocyanide, or yellow prussiate of potash, is a lemon yellow crystallized solid, and when pure is non-poisonous, which is exceptional in the case of cyanides. It contains three molecules of water. It may be made by treating iron or iron oxides with potassium cyanide, or by melting potassium carbonate and adding gradually a mixture of iron filings and refuse animal matter. It is freely soluble in water, dissolving in three or four parts at ordinary temperatures. When heated it loses water and is decomposed into potassium cyanide, nitrogen and iron carbide.

Potassium ferricyanide, or red prussiate of potash, may be formed by treating the ferrocyanide with chlorine, which unites with one atom of potassium, forming potassium chloride. It contains no water of crystallization and forms large dark red crystals which dissolve in water, forming a deep red unstable solution. In an alkaline solution it acts as an oxidizing agent, tending to form the ferrocyanide and is used in dyeing.

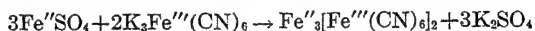
Ferric ferrocyanide, $\text{Fe}_4'''[\text{Fe}''(\text{CN})_6]_3$, known as Prussian blue, is formed by adding a ferric salt solution to potassium ferrocyanide and appears as a dark blue precipitate.



Ferric ferrocyanide is used in a more or less pure form as Prussian-, Berlin-, Paris- or mineral-blue in water and oil colors and in printing fabrics; dissolved in oxalic acid solution it is used as ink and as laundry blue, but if used in the last manner the clothes must be thoroughly rinsed or the iron compound

reacts with the soda of the soap and produces rust. Ferric salts produce no precipitates with potassium ferricyanide, which serves as a test for ferrous iron.

Ferrous ferricyanide, $\text{Fe}_3'' [\text{Fe}''' (\text{CN})_6]_2$, or Turnbull's blue is formed by adding potassium ferricyanide to a solution of ferrous sulphate or any soluble ferrous salt.



430. The Reactions that Serve as Common Tests to distinguish between ferrous and ferric iron may be summarized by the following tables:

<i>Add</i>	<i>To a Ferrous Salt</i>	<i>To a Ferric Salt</i>
Potassium ferrocyanide	whitish precipitate	Prussian blue
Potassium ferricyanide	Turnbull's blue	no precipitate
Potassium sulphocyanate	no change	dark red liquid
Ammonium hydroxide	greenish	red brown

NICKEL

431. Occurrence. Nickel comes from the Sudbury district of Ontario, Canada, and from New Caledonia. The metal is derived chiefly from nickel bearing iron ores, such as pyrrhotite, or from nickel blende, NiS , or from kupfernicker, NiAs , as found in Saxony and Bohemia. The metal is reduced according to the nature of the ore, usually by complicated processes. The ore is roasted and smelted in blast furnaces producing a matte containing nickel, copper and iron. The iron is removed in converters and the remaining product contains about 80% of nickel and copper with about 20% of sulphur. This mixture is reduced by various processes, one of which is the melting of the mass with sodium sulphide, while the copper sulphide and iron sulphide are separated after one or two more roastings. The nickel sulphide is then roasted to the oxide and the latter is reduced by fusing with charcoal in graphite crucibles.

432. Properties. Pure nickel is a grayish white metal with a slightly yellow appearance. It is very hard, but malleable and

ductile, if a little magnesium is added. Its specific gravity is about 8.6, varying somewhat with its treatment. It does not change in air at ordinary temperatures, but absorbs oxygen at red heat. It reacts rapidly with nitric acid but slowly with sulphuric acid or hydrochloric acid. Like iron it is magnetic and in contact with concentrated nitric acid, it becomes passive to the action of the acid. When finely divided, it combines with carbon monoxide at 100° forming nickel carbonyl, $\text{Ni}(\text{CO})_4$, which is solid at -25° and deposits pure nickel when heated.

433. Uses. Nickel is used in various alloys.

COPPER-NICKEL ALLOYS

<i>Alloy</i>	<i>Copper</i>	<i>Nickel</i>	<i>Zinc</i>	<i>Other Constituents</i>	<i>Uses, etc.</i>
Nickel coins	75 0	25			
English German silver	61.8	19 1	19 1		
Berlin Argentan	52 0	26 0	22 0		
Sheffield German silver	57 0	24 0	19 0		
Platinoid				A German silver with 1 to 2 per cent of tungsten	High electrical resistance

Monel metal consisting of nickel, 67.8%; copper, 28%; manganese, 2.5%; iron, 1.5%; vanadium 0.2% has the luster of silver, the strength of steel, does not corrode in moist air nor when exposed to the action of other agents that corrode most metals, resists acids, takes a high polish, may be molded or rolled to any shape, is very compact and is excellent for making springs.

Nickel may take the place of cobalt in the acid resisting alloys shown in §436 or may enter into a special copper nickel alloy containing copper 45 to 55%, nickel 29 to 35%, lead 1 to 3%, zinc 5 to 9%, iron 4 to 8%, silicon $\frac{3}{4}\%$ or less.

Nickeloid is nickel plated zinc, while nickel steel is steel containing 2 to 4% of nickel, used as armor plates for battleships.

Nickel is used in nickel plating very extensively, where the bath is usually nickel ammonium sulphate, the anode is pure nickel, otherwise it is the same as silver plating.

COMPOUNDS OF NICKEL

434. Nickel Forms Two Series of Compounds, nickelous where the metal is bivalent and nickelic where it is trivalent. Among the more important compounds are *nickelous chloride* NiCl_2 , which is formed by the action of chlorine on nickel filings. Golden yellow scales are obtained which give a green solution when boiling water is added. It may then be recrystallized to green crystals, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$. *Nickel sulphate*, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, forms emerald green prisms that are soluble in three volumes of water at 10° . *Nickel nitrate*, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, is formed when nitric acid reacts with metallic nickel, the equation being similar to that for nitric acid on copper. Large dark green crystals are formed that are soluble in two parts of water. They are not deliquescent in dry air, but melt at 56.7° in their water of crystallization. *Nickelous hydroxide*, $\text{Ni}(\text{OH})_2$, is an apple green, insoluble precipitate formed when a soluble hydroxide is added to a solution of a nickelous salt, and serves as a test for the presence of nickel. Nickel salts are used as the catalyzer in the hydrogenation of fats and oils. See §558.

COBALT

435. Occurrence and Preparation. Cobalt occurs with arsenic as smaltite, CoAs_2 , and as cobalt glance in CoAsS , or $\text{CoS} \cdot \text{CoAs}_2$. Iron and nickel often replace part of the cobalt. The ore is roasted and the product is dissolved in hydrochloric acid and treated with calcium hypochlorite, calcium hydroxide, and hydrogen sulphide which remove the other metals, and then, with calcium hydroxide, to precipitate cobalt hydroxide, $\text{Co}(\text{OH})_2$. This is converted into the oxide from which the metal may be obtained by heating in a current of hydrogen.

436. Properties and Uses. Cobalt, when pure, is white with a tinge of red. Its specific gravity is about the same as that of nickel. It is magnetic, malleable and tenacious. It melts at a temperature lower than that required for iron and dissolves in nitric acid. It is less tough than iron.

Cobalt is now being used to some extent to make alloys for cutting tools. One formula shows cobalt 35 to 65%, carbon 2 to 5%, chromium from 15 to 40% and tungsten 11%. Another formula shows cobalt from 40 to 60%, carbon 2 to 5%, chromium 20 to 35%, tungsten 5 to 20% and iron 1 to 15%.

Acid resisting alloys containing cobalt are made of cobalt 80%, molybdenum 10%, iron 10% or part of the iron is replaced by manganese up to 4%.

It is also used to a limited extent in electro-plating.

437. Cobalt Compounds, like those of iron and nickel, are of two kinds, cobaltous when the metal is bivalent, and cobaltic when trivalent.

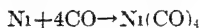
Cobaltous Chloride, CoCl_2 , is a red crystalline solid, containing six molecules of water, and formed when hydrochloric acid acts upon cobalt carbonate. When heated the crystals turn blue. If a very dilute solution is used as ink, the writing is invisible but becomes blue when moderately heated or brown when strongly heated. If the heating is only moderate the blue writing may be made to disappear by breathing upon it. *Cobaltous hydroxide*, $\text{Co}(\text{OH})_2$, is made as most hydroxides and is oxidized to *cobaltic hydroxide*, $\text{Co}(\text{OH})_3$, on standing in air. When heated they form respectively, *cobaltous* and *cobaltic oxide*, CoO and Co_2O_3 . *Cobalt sulphide*, CoS , is a black precipitate formed when ammonium sulphide is added to a solution of a cobaltous salt. *Cobaltous cyanide*, $\text{Co}(\text{CN})_2$, is a dirty red insoluble compound formed by adding potassium cyanide to a solution of a cobaltous salt. Smalt is a blue pigment made from cobalt glass, where a cobalt compound is heated with potassium carbonate and

quartz. It is then finely powdered. It does not change color in sunlight and is unaffected by acids and alkalies.

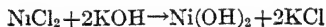
438. Problems.

1. How much carbon monoxide is required to reduce five tons of Fe_2O_3 ? (§416).

2 Show the quantitative formation of 40 grams of nickel carbonyl



3 How much nickel chloride is required to react with potassium hydroxide to form 60 grams of nickel hydroxide?



CHAPTER XX

ALUMINUM, TIN AND LEAD

ALUMINUM

439. Comparison of the metals of this chapter.

<i>Metal</i>	<i>At. Wgt</i>	<i>Valence</i>	<i>Specific Gravity</i>	<i>Melts</i>	<i>Boils</i>
Al	27 1	3	2 56—2 8	658 7°	1800°
Sn	118 7	2,4	7 —7 3	232°	1525°
Pb	207 2	2	11 35	327°	1580°

Although aluminum is found in group 3 of the Periodic System, and tin and lead are found in the fourth group, they will be described in the same chapter, since they are all common and well-known metals.

440. Occurrence and Preparation. Aluminum is the only common metal of the third group, and occurs widely distributed but always combined, as in feldspar, mica, cryolite, bauxite, clay, slate, corundum, etc., constituting in all about 7.5% of the earth's crust. Common alum is a double sulphate of aluminum and potassium, from which aluminum was first derived.

Various methods of extracting aluminum from its ores have been used, but the expense of obtaining this important metal was so great that its use was formerly impossible. The metal is now prepared by the *Hall process* by electrolyzing aluminum oxide, Al_2O_3 , commonly called alumina. The operation is conducted in large rectangular iron pots lined with carbon. (Fig. 125.) The pot serves as the cathode while the anode is formed from a number of graphite rods hung from a copper rod. Some powdered cryolite is introduced, the anodes are lowered and the current is passed, fusing the cryolite, after which more cryolite

is added and the aluminum oxide is stirred in. The resistance decreases after the addition of the oxide which is decomposed into aluminum and oxygen. The oxygen goes to the anode with which it combines, forming carbon dioxide. As a result the anodes wear away and must gradually be lowered into the bath and finally renewed. When the resistance increases it indicates that more aluminum oxide must be added. The amperage is 250 to 300 for each carbon rod. The process is continuous and the aluminum is siphoned out at intervals. The cryolite is not decomposed and serves merely as a solvent for the aluminum oxide. Before the Hall process was used aluminum cost about

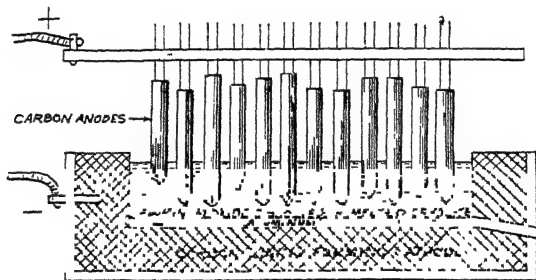


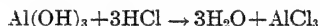
FIG 125. Manufacture of Aluminum by the Hall Process

\$12 per pound, while the present cost is usually less than 40 cents. Aluminum is also prepared by the electrolysis of aluminum chloride, using aluminum chloride and sodium chloride as an electrolyte while the aluminum chloride is supplied continuously at such a rate as to keep the bath saturated. The aluminum is kept in a molten condition by the heat developed and the chlorine is drawn off separately. Clay is not used as a source of aluminum because of the presence of iron, silicon, etc., which modify the properties of the metal. If suitable methods could be devised for extracting aluminum from ordinary clay, the price of aluminum could be greatly reduced.

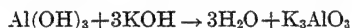
441. Properties. Aluminum is a very light metal. It is white in color and has a high luster. It is as strong as cast iron, malleable, ductile, sonorous and a good conductor of heat and electricity but lacks toughness and resistance to strains. It is not oxidized readily by dry or moist air, but after it is oxidized it should not be polished, since the coating of oxide is removed and fresh surfaces are exposed for oxidation. Aluminum does not act readily upon water even at elevated temperatures. If heated in thin strips it burns in oxygen to the oxide. It reacts easily with hydrochloric acid forming the chloride, and with potassium hydroxide or sodium hydroxide forming aluminates and evolving hydrogen. Sulphuric, nitric and organic acids do not act upon it at ordinary temperatures, but sulphuric and nitric acids act upon it at high temperatures, forming the sulphate and nitrate respectively. The reaction with potassium hydroxide may be written



Salts of aluminum act as either base formers or acid formers. If aluminum hydroxide is mixed with an acid it acts as a base



but if it is mixed with a base it acts as an acid



If sodium hydroxide is used instead of potassium hydroxide, sodium aluminate instead of potassium aluminate will be formed.

442. Goldschmidt's Thermit Process is now used quite extensively for the reduction of metallic oxides. It consists essentially in mixing an excess of the metallic oxide with one or more powdered metals or metallic alloys, and igniting the mixture at one point, from which the ignition proceeds throughout the mixture, with complete oxidation of the reducing element, forming a fluid slag, while the original oxide is reduced to a

metal, free, or practically free, from the element used as the reducing agent.

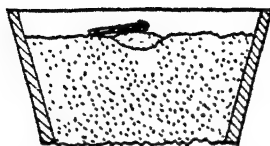
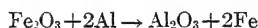


FIG. 126. Igniting Thermit

As a simple illustration ferric oxide and powdered aluminum may be ignited by the use of a piece of magnesium ribbon. (See Fig. 126.)



The aluminum has greater heat of oxidation than almost any other metal and since the aluminum oxide is not volatile the heat is not lost and the temperature produced will reach 3000° or more.

The process is applied practically in welding; e.g., an iron rail, where the joint is packed with the mixture and ignited. The iron goes to the bottom and the aluminum oxide to the top, the heat produced being sufficient to bring about the weld, with a resulting average strength of 30 tons per square inch, but which may be increased by the addition of 1% of nickel. Other uses for thermit are found in the production of carbon free metals and alloys, such as chromium, manganese, molybdenum, ferro-titanium, ferro-vanadium, ferro-boron, manganese-copper, manganese-zinc, manganese-titanium, chromium-manganese, etc., which are of great value in the steel industry.

Instead of using aluminum a mixture of 60 parts of aluminum and 40 parts of calcium may be used; or 2 parts of calcium and 1 part of silicon; or a mixture of magnesium and silicon.

443. Other Uses of Aluminum. Aluminum is made into scores of articles where strength, lightness and attractive appearance are desired. The number of articles made from aluminum is constantly increasing.

Aluminum is used to some extent for covering grate bars in locomotives. The coating is made about 0.1 millimeter thick and the coated bars last about 4 times as long as the bare ones.

A reinforced aluminum cable consisting of one part of steel to 4 parts of aluminum, has been shown to be equivalent to a

copper cable in carrying capacity and tensile strength. The aluminum must be at least 99% pure. It is also used in steel making, less than 1 part in 1000 being required to combine with the gases in the steel, thus preventing blow-holes.

The following table shows some of the common

ALUMINUM ALLOYS

<i>Alloy</i>	<i>Copper</i>	<i>Aluminum</i>	<i>Magne- sium</i>	<i>Others variable</i>	<i>Uses, etc.</i>
Magnalium		70-90	10-30		Very strong, non-corrosive, and can be turned in a lathe. Harder than aluminum but not as heavy.
Aluminum bronze	90 0-98	2-10			Tensile strength 96,434 pounds per square inch. Can be used for yacht hulls. Takes high polish, and is very acid resistant.
Aluminum Silicon		80-90		Si 10-20	Specific gravity less than 2.7, suitable for parts of internal combustion engines

Some other aluminum alloys are: aluminum zinc, aluminum copper, aluminum nickel, iron aluminum, etc.

Aluminum is used also as foil, powder and aluminum coated paper. It is used in some explosives such as ammonal. It is used to make hydrogenite which consists of aluminum powder, mercuric chloride and potassium cyanide which evolves hydrogen when brought into contact with water. The world

production of aluminum amounts to at least 225,000 metric tons annually.

An alloy consisting of Al, 7%; Zn, 24-25%; Cu, 3%; Mg, small amounts, resists corrosion while if the Al is increased to 91%, copper to 6.5% and the zinc reduced to 2% the alloy becomes very ductile and suitable for airplane and automobile parts.

The soldering of aluminum has presented many difficulties. Some of the recent aluminum solders and fluxes that have been put upon the market are shown in the following table:

AL SOLDER

	Cu	Al	Zn	Sn	Pb	Brass	Ag	Sb
1	15-2	28	375-365	33*				
2			20-70	15-60	10-60**			
3			36	61		1-2	1-2	
4	4	4	4	60	12		10	2***
5			238	762				

*First melt the tin, then add Cu and stir till melted. Then add Al and Zn

**First melt part Sn: add Pb then Zn, then more Sn and Pb, mixing and molding

***Melt Ag, Cu and Al in graphite crucible lined with magnesia: add others gradually stirring with a carbon rod covered with magnesia. When fused add 20 parts of borax, stir: remove the scum and cast in molds lined with magnesia

FLUXES FOR AL SOLDERING

Powdered rosin, 75%; vaseline, 20%; ammonia, 5%.

Stearic acid, 64%; borax, 8%; rosin, 8%; powdered cinnamon bark, 20% for such a solder as No. 5.

A recent British patent flux for welding aluminum gives as a suitable mixture KCl, 45%; NaCl, 30%; KF, 7%; LiCl, 15% and sodium or potassium pyrosulphate or pyrophosphate

1-10%. The last named substance is added as an activating agent and reacts with the other substances only in the presence of Al_2O_3 . The materials are all melted together in a vessel free from metallic oxide soluble in the flux, and after solidifying the homogeneous mass is powdered.

Aluminum may be coated with zinc by first coating the surface with a flux consisting of sodium chloride 1 part, sodium fluoride 3 parts, and potassium chloride 5 parts. The zinc coating is then placed by sherardizing or by vapor galvanizing. See §500.

444. Aluminum Oxide, Al_2O_3 , called alumina, occurs native in many localities as corundum, or as an opaque corundum containing iron oxide known as emery, and, next to diamond is the hardest natural product known. As an abrasive it has been displaced to a large extent by carborundum or crystolon and to a smaller extent by alundum, all manufactured products, which are harder than corundum. However, natural corundum is the only abrasive suitable for polishing glass.

Alundum is made from a mixture of bauxite and coke, the principal ingredient being Al_2O_3 . It is an electric furnace product, and comes from the furnace in large masses, which are crushed under heavy pressure, the crushing strength being $7\frac{1}{2}$ tons per square inch. Alundum melts at 2020°C .; it has a thermal conductivity 2.1 times that of fire bricks, and a low electrical conductivity. Alundum is used in various ways, such as in wheels for cutting glass, for grinding steel, iron, nickel, etc., as crucibles, filter crucibles, combustion boats, etc.

Crystolon is silicon carbide, very similar to carborundum. (See §346.) It is made in the electrical furnace (See Fig. 127) which is charged with silicon dioxide, SiO_2 , and coke, with small quantities of saw dust and salt. The materials do not melt, but the oxygen of the SiO_2 is driven off and the silicon combines with carbon. It is characterized by extreme hardness and sharpness of grain. Crystolon is used in muffles, as linings in electrical furnaces, as pyrometer tubes, as wheels for cutting

glass, as sharpening stones, etc. A comparison of some abrasives is shown in Fig. 128.

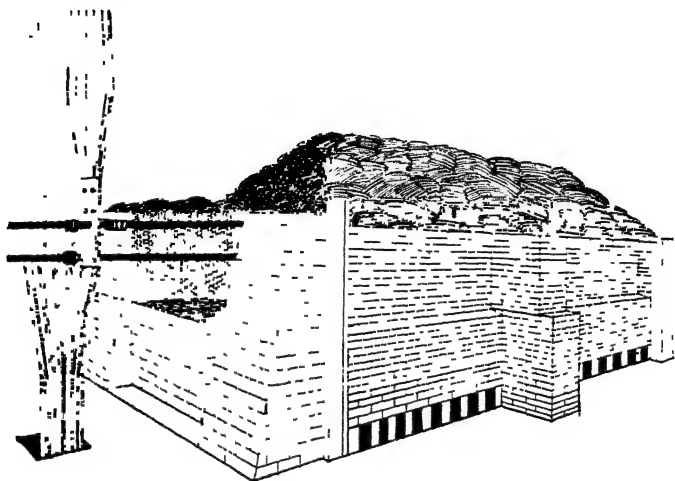


FIG. 127. A Crystolon Furnace.

Aluminum oxide may be prepared by heating the hydroxide or by burning the metal. It is a white powder, insoluble in water

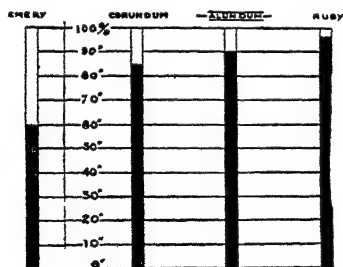
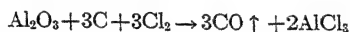


FIG. 128. Comparison of Abrasives.

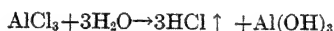
and not decomposed by heat. It fuses in the oxyhydrogen flame or in the electric furnace. It is used to polish hard metals, plate glass, etc. The pure crystallized varieties of aluminum oxide are called corundum, many of which are transparent, and when colored by various oxides are highly prized as gems, among which may be mentioned sapphire, topaz, ruby, amethyst, emerald, garnet, turquoise, etc. some of which are now made artificially.

Sometimes gems are artificially colored by bleaching them in a solution of tartaric acid and ferrous sulphate or copper sulphate after which they are dyed by placing them in alcohol to which is added by degrees a water soluble aniline dye.

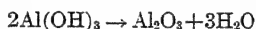
445. Aluminum Chloride, AlCl_3 , is a white or yellowish crystalline solid formed when a stream of chlorine is passed over an incandescent mixture of aluminum oxide and charcoal, at a temperature of 1600° to 2000° .



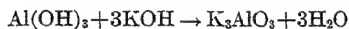
It fuses and volatilizes a little above 190° . It dissolves in water, evolving considerable heat and if the temperature is raised hydrochloric acid is given off and aluminum hydroxide is formed.



446. Aluminum Hydroxide, $\text{Al}(\text{OH})_3$, formed as above or by adding ammonium hydroxide to aluminum chloride is a white jellylike solid, resembling starch paste, insoluble in water. It dries in the air and when heated to high temperatures, water is given off and aluminum oxide is formed.

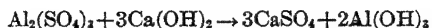


When aluminum hydroxide reacts with sodium hydroxide or potassium hydroxide, the aluminate of the metal and water are formed.



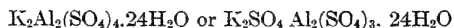
447. Aluminum Sulphate, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, may be made from aluminum hydroxide and dilute sulphuric acid, the mixture being evaporated to crystallization. It is soluble in two parts of cold water. When heated it first gives off water and is then partly decomposed to sulphur trioxide and aluminum oxide. It is used for sizing paper, as a mordant in dyeing, etc.

A mixture of aluminum sulphate and slaked lime is used for settling water,



but if the water contains an abundance of lime none need be added to cause the water to settle. Iron sulphate may be used instead. The lime precipitates the iron as ferrous hydroxide which is oxidized to ferric hydroxide, and this coagulates the suspended matter.

448. Alums. More widely known than aluminum sulphate are the substances known as alums of which there are several kinds. They are double sulphates containing 24 molecules of water of crystallization. Common alum is made by stirring a concentrated solution of potassium sulphate into a concentrated solution of aluminum sulphate which gives a double sulphate having the formula



This is known as alum or potassium alum. Alum is soluble in water, especially when hot, from which the crystals are deposited on cooling. When alum is heated it loses its water of crystallization and becomes a porous white powder known as dehydrated or burnt alum. Other double sulphates give different kinds of alums, among which may be mentioned ammonia alum made from ammonium and aluminum sulphates, sodium alum from sodium and aluminum sulphates, etc. Chrome alum is a double sulphate of chromium and potassium, iron alum of iron and potassium, manganese alum of manganese and potassium. A number of other alums are known, and they may be said to consist of the sulphate of a trivalent metal as aluminum, iron, chromium or manganese, united with the sulphate of a univalent metal as potassium, sodium, lithium, rubidium, caesium, silver, and copper, (ous) the crystal containing 24 molecules of water of crystallization. Alum and aluminum salts are used as mordants in dyeing and calico printing. Many dyes wash out unless made "fast" or insoluble by the addition of a metallic salt. The cloth is first dipped into a solution of the aluminum salt and then into the dye. An insoluble metallic compound known as a "lake" is formed and the cloth will hold its color. Alum is also used in

tanning, in medicine, in purifying water, in making mixtures for rendering cloth, wood, etc., fireproof, in making baking powders, as a size for paper, etc.

For more detailed descriptions of dyes and dyeing see Chapter 31.

449. Bricks, Pottery, etc. Ordinary clay, formed chiefly from the decomposition of feldspar is an impure aluminum silicate containing the silicates of sodium and potassium, while pure clay, or kaolin, is a pure hydrated aluminum silicate having the formula $\text{Al}_2\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$, but it is hard to obtain it absolutely pure in nature and ordinary clay always contains many impurities. (Fig. 129.) The decomposition is brought about by the



FIG 129. Kaolin Deposits.

action of the atmosphere, the dissolving out of soluble matter, the expansion and contraction due to changes of temperature, and the action of organic acids found in plants that become embedded in the soil. Analyses of normal clays show SiO_2 , 53 to 74%; Al_2O_3 , 20 to 30%; Fe_2O_3 , 5 to 9%; CaO , 0.36 to 4%; MgO , 0.31 to 2%; Na_2O and K_2O , up to 3.64%; SO_3 up to 1%; CO_2 and H_2O up to 17%. If the clay contains more than 5% of CaO and MgO together it is called a limy clay. *Shale* is

clay hardened by pressure. *Slate* is a form of shale in which a fine, even and parallel cleavage has been developed by pressure.

Bricks are blocks of clay, molded when wet and then burned.

Adobe bricks are sun dried and not burned. They may be used where the climate is warm and dry but since they are reduced back to clay by the action of water they are not suitable for outside use in a moist climate. Burned bricks may not be changed back to clay by the action of water, but when they are pulverized to a powder and mixed with water, or with water, sand and lime they may be made into a good hydraulic cement.

Fire Bricks are made from clays that will withstand an intense heat. They are tempered by adding to the raw clay a portion of clay that has been burned until it no longer shrinks. The material is ground with coarse sand or feldspar, molded and burned. Fire bricks are used for the linings of furnaces, or the fire clay may be molded into retorts for gas makers, for zinc smelting, or pots for glass makers, etc.

Drain Tile is made from clay as used in brick making, but since this gives a porous tile it is not suitable for sewer pipes so that for the latter, fire clay is used. Fire clay should be dug in the fall and exposed to frost during the winter, the weathering making it more suitable for use in the spring.

Roof Tiles are made from either brick clay or fire clay. After burning they are glazed and are then put back into the ovens and left until the glaze begins to run. The glaze may be made from a mixture of lead oxide and calcined flints. When iron filings are used the glaze is black, while copper slag gives a green glaze and smalt gives a blue color. Tile is considered the best roofing. It is a non-conductor of heat making the building cooler in summer and warmer in winter. Buff tile does not absorb the heat of the sun, and there is no tendency to crack with changes of temperature. In addition to these advantages the surface of the tile is smooth and very little dirt sticks to the surface so that where rain water is used it is much cleaner if collected from a tile roof than from either slate or shingles.

Glazed Bricks are made in a manner similar to glazed tile, the glaze being pure white clay. *Vitreified paving bricks* are made from clays free from sand, the clay being very finely pulverized and the temperature of burning being 800° to 1000°.

Kaolin is used for the finest kinds of pottery. Other materials such as sand, feldspar, quartz, etc., are added to the kaolin to diminish shrinking when baked. These substances also diminish plasticity.

Porcelain is the finest kind of pottery and is hard, dense, white, and semitransparent except when thick. *Stoneware*, as the ordinary jugs, jars, etc., is similar to porcelain, but made of cheaper materials; *crookery* is a fine grade of stoneware, while if less pure materials are used it is known as earthenware, common pottery, or *terra cotta*. *Porcelain* and *stoneware* are semivitreous, while *faience*, etc. are porous. Most of these forms are glazed before being sold.

The *glazing for porcelain* consists of kaolin and quartz reduced to a fine powder and suspended in water into which the article is dipped, and then subjected to a second baking to fuse the glaze. *Faiences* made from plastic clay mixed with quartz, are glazed with a mixture of quartz, potassium carbonate and lead oxides. The glaze may be made opaque by adding tin oxide. Common pottery is usually glazed by throwing salt into the baking ovens before the baking is finished.

TIN

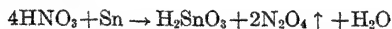
450. Occurrence and Preparation. The commercial source of tin is cassiterite or tin stone, SnO_2 , which is often accompanied by mispickel, FeSAs , and iron pyrites, FeS_2 , which must be removed before smelting. This is done by roasting, which changes the iron to the oxide that may be removed by washing.

The largest supply of the ore comes from the Malay States, the next important tin producing country being Bolivia, while the Cornwall district of England is third. The amount found in

the United States is very small, but a little has been shipped from South Carolina, South Dakota and Alaska.

The tinstone is reduced in a shallow blast furnace charged with ore and charcoal and only a moderate blast is used but the metal always contains iron. It may be reduced in a reverberatory furnace, the ore being mixed with 15 to 20% of anthracite or semibituminous coal, and heated strongly for three or four hours. Some lime is usually added to turn the coal ashes to slag which is skimmed off preferably before withdrawing the metal, as it is very free from tin and may be rejected. If the slag contains much tin it usually has to be resmelted several times at a high temperature with the addition of scrap iron or iron ore which is reduced in the operation, with the yield of a poorer quality of tin. The iron is removed by melting the tin on the sloping hearth of the reverberatory furnace, the tin melting first while the iron remains solid. The other impurities are then removed by oxidation either by thrusting green sticks into the melted tin, known as "boiling," or by pouring it from ladles in a fine stream, called "tossing," or by blowing air into the molten mass.

451. Properties. Tin is a white metal resembling silver. It is soft, malleable and ductile, but without great tenacity. It is harder than lead. Melted tin rapidly oxidizes to the white oxide of tin, SnO_2 , although it is unchanged in the air at ordinary temperatures. When a bar of tin is bent, a peculiar noise, called the cry of tin, is heard. Ordinary nitric acid poured upon tin converts it to metastannic acid, while red vapors of nitrogen tetroxide are evolved.



Very dilute nitric acid gives hardly any red vapors and the chief products are tin nitrate and ammonia. Concentrated hydrochloric acid converts it to stannous chloride, SnCl_2 ; hot concentrated sulphuric acid forms stannous sulphate, SnSO_4 , while sulphur dioxide is evolved. With sodium hydroxide or potassium hydroxide, hydrogen is evolved and an alkaline

stannate is formed. Tin may be precipitated from its solutions by zinc. It combines directly with chlorine forming stannic chloride, SnCl_4 . Tin sometimes changes into a gray, pulverulent, lighter modification, specific gravity 5.85, when kept at a temperature below 20° .

452. Uses of Tin. Thin clean pieces of sheet iron dipped into molten tin receive a coating of tin and are known as tin plate or tin. They are used for kitchen utensils, roofing, etc. Copper may be covered in the same way and is used for cooking vessels. Tin is used to coat pins, tacks, etc. It is rolled and hammered into tin foil and enters into several alloys.

TIN ALLOYS

<i>Alloy</i>	<i>Tin</i>	<i>Antimony</i>	<i>Copper</i>	<i>Other constituents</i>	<i>Uses, etc.</i>
Britannia metal	90 62	7 92	1 46		Variable in uses and composition The melting point increases with the lead
White metal	82 00	12.00	6 00		
Pewter	80 00			Lead 20 00	
Solder, fine	66 67			Lead 33 33	
Solder, tin	50 00			Lead 50 00	
Solder, plumbers'	33.33			Lead 66 67	

A soldering flux said to be suitable for soldering at temperatures as high as 400° is composed of zinc chloride, 65%; ammonium chloride 10%; with 25% of a mixture consisting of potassium chloride 56% and sodium chloride 44%.

453. Stannous Oxide, SnO , is not important. *Stannic oxide, SnO_2 ,* as found in nature occurs as hard transparent crystals of a yellowish brown or black color. Artificial stannic oxide is a faint yellow color when hot, and white when cold.

454. Chlorides. *Stannous chloride, SnCl_2 ,* prepared by heating tin in hydrochloric acid gas is a white or grayish substance, greasy and almost transparent. It fuses at 250° and boils at 600° . If tin is dissolved in hot concentrated hydro-

chloric acid and the liquor is evaporated and cooled, transparent greenish crystals, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, known as tin crystals or tin salt are formed. Stannous chloride dissolves in a little water forming a clear solution which becomes cloudy if much water is added, forming an oxychloride. Stannous chloride reduces mercuric chloride to mercurous chloride and is itself oxidized to stannic chloride.



If an excess of stannous chloride is added the rest of the chlorine is taken from the mercurous chloride and metallic mercury appears. Stannous chloride is used as a mordant in dyeing and produces brilliant colors. (See Chapter 31).

Stannic chloride, SnCl_4 , formed when tin foil is thrown into jars of chlorine gas, is a liquid giving white fumes in the air. It may be prepared by passing chlorine gas over tin in a small retort, giving a yellow liquid that is decolorized by adding a little mercury. It boils at 120° and has a specific gravity of 2.28. It is formed when tin is dissolved in aqua regia or when chlorine is passed into stannous chloride. The action of chlorine upon tin is the basis of the process commonly used to recover tin from tin scrap. The scrap plate is cleaned, dried and exposed to dry chlorine gas giving the stannic chloride, which is used in mordanting. By a recent British patent, tin is recovered from scrap by electrolysis.

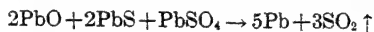
LEAD

455. Occurrence and Preparation. Lead, known from antiquity, does not occur free in large quantities, but is found widely distributed in compounds. The annual amount produced is over 800,000 tons of which the United States produces more than one-fourth. The chief source of the metal is galena, PbS , found in abundance in several of the states of the central west and far west of the United States, in Germany, Spain, New South Wales, England, Mexico, etc.

The sulphide is roasted in blast furnaces. The ore, mixed with iron, a flux and coke, is heated and the lead is set free, while the iron forms ferrous sulphide. If the ore is rich in lead it is usually heated in a reverberatory furnace in contact with air. Part of the lead sulphide is oxidized to the oxide, part to the sulphate.



The sulphide, oxide and sulphate are then heated to a higher temperature without air and the reaction is as follows:



The ore may be reduced by electrolysis. The bottom of the reduction pan is made the anode, crushed lead sulphide is the cathode and dilute sulphuric acid is the electrolyte. Since the acid is electrolyzed as well as the lead sulphide, the sulphur is evolved as hydrogen sulphide and the spongy lead collects at the bottom of the pan. If the ore is very poor it is treated for 24 hours at red heat with lime and air. A mixture of lead sulphate and calcium sulphate is produced and this is mixed with coke and reduced in a closed furnace.

456. Properties. Lead is a blue gray metal with a brilliant luster when freshly cut but it soon tarnishes. It is soft, malleable and ductile, but is not tenacious enough to be drawn into very fine wires, although it may be rolled into sheets. Melted lead contracts on cooling. Heated in air lead changes to the oxide, PbO . Pure water, when air is present dissolves a little lead, while if decaying organic matter is present the lead dissolves readily. This explains the presence of small amounts of lead in rain water, where lead spouting and tanks are used. Cheap tinware containing lead should not be used for cooking. The presence of lead salts in water makes the water unfit to use since the salts are poisonous. If the water contains sulphates or carbonates the action soon ceases as they form a protective coating on the lead, so that lead pipes may be used for hard water.

Concentrated boiling hydrochloric acid slowly dissolves lead. Dilute sulphuric acid does not act upon it but concentrated sulphuric acid reacts with it to some extent and lead is, therefore, often found in sulphuric acid. (See §297.)

Nitric acid, if comparatively dilute, reacts with lead forming lead nitrate, $\text{Pb}(\text{NO}_3)_2$. Acetic acid, which is contained in vinegar, fruit acids, etc., reacts with lead so that the use of lead vessels is unsafe. Lead is easily replaced from solutions of its salts by zinc.

An illustration of lead poisoning is seen in painters' colic.

457. Uses of Lead. Lead is used for shot, for water and gas pipes, and as sheet lead is used on roofs, as linings for troughs, etc. It is used in type metal and other alloys.

The addition of the arsenic to the melted lead causes the melting point to be lowered. Hence when the lead-arsenic alloy flows through the sieve at the top of the shot tower (about 200 feet high) the mixture remains liquid long enough to enable the drops to become spherical. The falling shot drops into a tank of water at the bottom of the tower, thus preventing flattening.

LEAD ALLOYS

<i>Alloy</i>	<i>Lead</i>	<i>Antimony</i>	<i>Tin</i>	<i>Other Constituents</i>	<i>Uses, etc.</i>
Type metal	70 0	18 0	10 0	Cu 2 0	For stereotyping For slowly revolving axles
Type metal	82 0	14.8	3.2		
Bearing metal	84 0	16.0			
Bearing metal	60.0	20.0	20 0	As 0.2 to 0.40	
Shot metal	99 6				

Lead chambers and evaporating pans are used in the manufacture of sulphuric acid. Spongy lead is used in storage batteries. It is not used in "lead" pencils although lead will leave a mark when drawn over paper. (See §248.)

LEAD COMPOUNDS

458. Oxides. Lead forms four or five distinct oxides, the suboxide, Pb_2O ; the monoxide, PbO ; the sesquioxide, Pb_2O_3 ; the tetroxide, Pb_3O_4 ; and the dioxide, PbO_2 .

Lead monoxide, PbO , may be made by heating lead nitrate, or by heating lead in air to high temperatures. It is a yellowish powder known as massicot, or a crystalline mass called litharge. It is used in making flint glass, oils, varnishes, and for certain lead compounds. It is easily reduced by hydrogen, carbon, or carbon monoxide. It is slightly soluble and gives an alkaline reaction.

Lead Tetroxide, red lead, or minium, Pb_3O_4 , is a red powder made by heating lead oxide in the air to 350° . The amount of oxygen varies slightly and so does the color. Heated to a high temperature it loses oxygen and becomes lead oxide. It is used in making paints and in plumbing and gas fitting to make tight joints. It seems to be a chemical compound.

Lead Dioxide, PbO_2 , is a brown powder formed when red lead is treated with dilute nitric acid. It is insoluble in water. It loses half its oxygen when heated and is reduced by such substances as hydrochloric acid.

459. Lead Carbonate, PbCO_3 , may be formed by adding a solution of ammonium carbonate to a solution of lead nitrate. If the carbonate of sodium or potassium is used, basic carbonates of varying composition are formed, the most important being white lead, $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$. It is a heavy white powder used as paint when mixed with linseed oil, with or without coloring matter. It is made by several processes among which the most important are the following:

460. The Dutch Process. In the Dutch process sheets of lead made into buckles are exposed to the action of vinegar, air and carbon dioxide formed by the decay of organic matter, such as horse manure. (Fig. 130.) The lead is placed in an earthenware vessel with the vinegar in the bottom, not touching the

lead. The vessels are then placed upon the organic matter. At first an acetate is formed, and this is changed to the basic carbonate by the action of the carbon dioxide. The operation

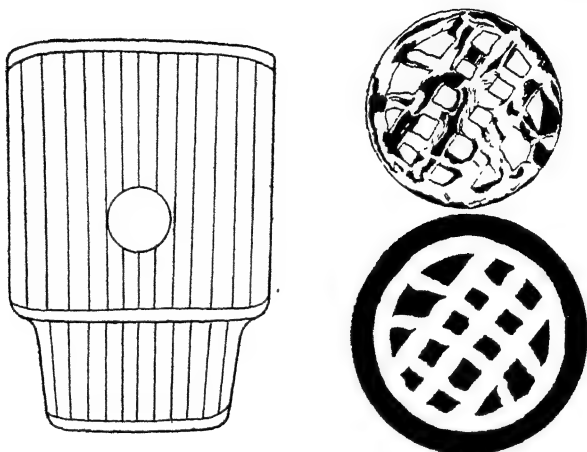


FIG. 130. Lead Buckles and Corroding Pot.

requires two or three months. (Fig. 131.) Fig. 132 shows a white lead grinding machine. The manufacture and use of white lead is, however, now prohibited in France.

461. In the electrolytic process the method is essentially the action of sodium acid carbonate on lead hydroxide. The anode is lead, the cathode is copper and the electrolyte is a solution of sodium nitrate. Nitric acid formed at the anode unites with the lead to form lead nitrate, while sodium at the cathode forms sodium hydroxide which reacts to form the lead hydroxide and sodium nitrate. The hydroxide is then treated with sodium acid carbonate. The process is very rapid and is said to be satisfactory. If lead sulphide forms in the carbonate the paint turns dark.

462. In the Carter Process, the lead is atomized by being melted and blown through a nozzle while steam is blown



FIG. 131. Removing the Lead Buckles.

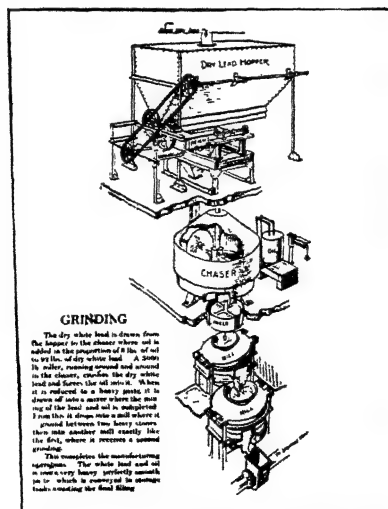


FIG. 132. Grinding White Lead.

through it. The lead is divided into very fine particles that are slightly oxidized. (Fig. 133.) Then about 4000 pounds are placed in a wooden cylinder 6 feet in diameter and 10 feet long, that revolves slowly on a horizontal axis. The lead is treated with dilute acetic acid and carbon dioxide, the acid being sprayed in at intervals while the carbon dioxide is admitted through an

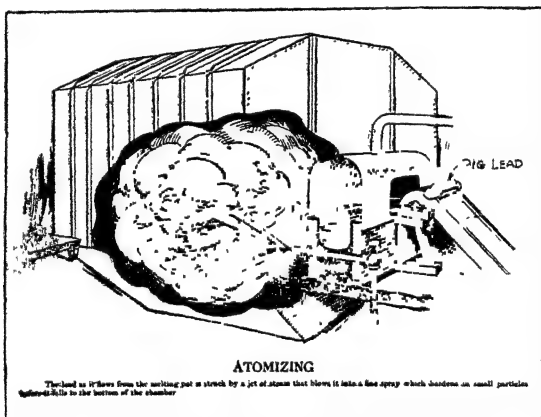


FIG. 133. The Carter Process—Atomizing the Lead

opening in the center of the head. The carbon dioxide is made from the complete combustion of coke. The lead is kept moist by water. (Fig. 134.) When the acetic acid acts upon the lead, various basic lead acetates are formed. The carbon dioxide acting upon these forms basic lead carbonate and re-forms acetic acid, which may be used over and over upon the lead and lead oxide until it is all used and the process is complete. As the cylinder revolves the mixture is carried part way up and then rolls down, grinding the carbonate from the surface of the lead and reducing it to a very fine powder. No external heat need be applied since the heat of the action is sufficient, the temperature being about 145° . At the end of 15 days the carbonate is taken out, washed to remove the acetic acid or lead

acetate, then floated in water to remove any lead that may have been unacted upon. The carbonate is then run into tubs where it settles and the water evaporates. Before it is sold it is mixed with 8% of raw linseed oil so as to keep it pliable.

463. Other Lead Compounds. *Lead Sulphide*, PbS , as galena, is the source of lead and occurs in crystals resembling lead. It may be formed in the laboratory by hydrogen sulphide acting upon solutions of lead salts, a black precipitate being given.

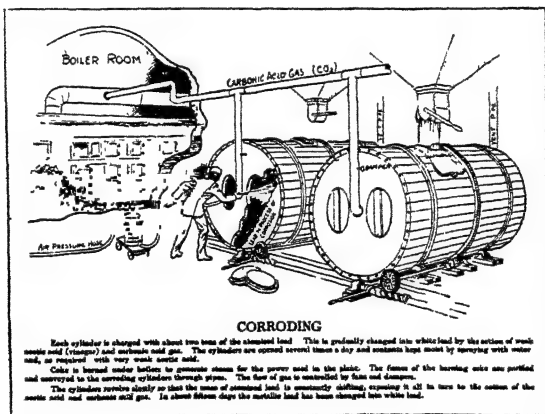


FIG. 134. The Carter Process—Corroding the Lead.

Lead Nitrate, $Pb(NO_3)_2$, formed by dissolving lead, lead oxide, or lead carbonate in nitric acid is a crystalline salt, easily soluble in water and is decomposed by heat into lead oxide and nitrogen tetroxide.

Lead Sulphate, $PbSO_4$, occurs in nature or is formed by the action of lead on sulphuric acid or by adding a soluble sulphate to the solution of a lead salt. It is nearly insoluble in water but is soluble in sulphuric acid, and reacts with nitric and hydrochloric acids. When heated to redness it loses sulphur trioxide.

Lead Acetate, $Pb(C_2H_3O_2)_2$, or sugar of lead, is formed when acetic acid acts upon lead or lead oxide. It is soluble in water

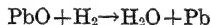
and is used to some extent in medicine in cases of ivy poisoning, etc. Probably the most effective remedy for ivy poisoning is to wash the blisters first with a 5% solution of carbolic acid, followed immediately (without drying) by a saturated solution of lead acetate. Usually three or four such applications will produce a cure.

Lead Chloride, PbCl_2 , is formed when hydrochloric acid or a soluble chloride is added to a cold solution of a lead salt. A white solid, soluble in hot water is obtained. This is one of the standard tests for lead.

Lead iodide, PbI_2 , and *lead chromate*, PbCrO_4 , are formed when a solution of a lead salt is added to potassium iodide and potassium chromate respectively.

464. Problems.

1. Write the quantitative equation where 10 grams of aluminum react with potassium hydroxide. (§441).
2. When carbon and chlorine react with 50 grams of aluminum trioxide how many grams of aluminum trichloride will be formed? (§445)
3. How much aluminum hydroxide can be formed from the aluminum chloride that is obtained in the preceding problem? (§445).
4. How much mercurous chloride will be formed when 25 grams of stannous chloride react with mercuric chloride? How much stannic chloride? (§454).
5. If 100 grams of lead oxide, PbO , are reduced, how much lead is obtained?



CHAPTER XXI

COPPER, SILVER, GOLD AND PLATINUM

In this chapter we shall study four metals, the first three being rather closely connected according to the periodic system, being found in the first group, while platinum occurs in an entirely distinct sub-group in group 8, but will be described in this chapter because of numerous similarities in properties and uses.

465. Comparison of the metals of this chapter.

<i>Metal</i>	<i>At. Wgt</i>	<i>Valence</i>	<i>Specific Gravity</i>	<i>Melts</i>	<i>Boils</i>
Cu	63 57	1,2	8 5 — 8 95	1083°	2100°
Ag	107 88	1	10.42—10 6	961°	2050°
Au	197 2	3	19 3	1063°	2500°
Pt	195 2	4	21 1—21 5	1755°±20°	—

COPPER

466. Occurrence. Copper, known for more than 2,000 years, occurs both free, as in the mines of Michigan, and combined as copper oxide, CuO , copper sulphate, CuSO_4 , copper carbonate, CuCO_3 , in the mines of Arizona, as cupric sulphide, CuS , cuprous sulphide, Cu_2S , and in various ores containing iron and copper combined with sulphur, having such formulas as CuFeS_2 , known as chalcopyrite, and Cu_3FeS_4 , known as bornite, as found in Montana. The compounds of copper are known as cuprous compounds where the metal acts as a uni-valent, and as cupric compounds where it is bivalent.

467. Preparation. Copper ore is crushed, washed to remove impurities and then treated according to the composition of the ore. The oxide and carbonate are easily reduced by being heated with coke which forms carbon monoxide and sets the copper free. If the ore is a sulphide or a double sulphide, the treatment

is more complicated. Concentration of copper ores by flotation is widely followed. See §355 for the method. The ore is roasted in a reverberatory furnace (see Fig. 135) where part of the sulphur is changed to sulphur dioxide and some of the sulphide is changed to the oxide. Any iron sesquioxide, Fe_2O_3 , produced by the roasting combines with part of the ferrous sulphide to form ferrous oxide, FeO , and sulphur dioxide. The ferrous oxide

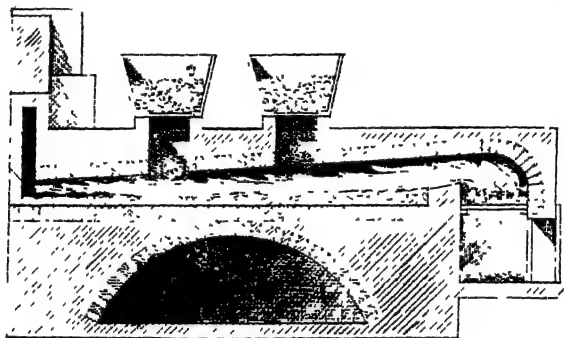


Fig. 135. Reverberatory Furnace for Copper.

with any calcium oxide, aluminum oxide, etc., that may be present unite with silicon dioxide that is present in the ore forming a slag; while the copper and the remaining iron and sulphur unite to form the matte which takes up the gold and silver if any is present, and sinks while the slag rises. The copper in the matte varies from 35 to 50% while in the slag it is about $\frac{1}{2}\%$. The slag is skimmed off through a hole at the end of the furnace opposite the fire box and is thrown on the dump after making sure that it is free from matte. The matte is removed from the side of the furnace through a hole that is closed with a clay plug. Neither slag nor matte is completely removed as the melted mass retains heat and causes the new charge to melt more rapidly.

The reverberatory furnace method is the best for fine ores and the blast furnace method for coarse ores. The blast furnace

is similar to that used for iron ores, (see §415) differing chiefly in size, shape, and materials used in construction. After the matte is drawn from either style of furnace it is taken to the converters or cast in molds. The converter is similar to that used in making Bessemer steel, (see §417) differing chiefly in the position of the tuyeres which are placed several inches above the bottom. The converters are often placed in a horizontal position instead of in a vertical position so as to have less depth, thus saving both blast and material which would otherwise be blown out. (Fig. 136.) The elements to be removed by the blast are from 50 to 65% of the whole charge and are chiefly sulphur and iron instead of about 6% as when iron is converted to steel. The time, therefore, to convert a ten ton charge is about 2 hours instead of about 15 minutes as in the case of iron. The linings of the converter must be renewed frequently and usually last from 3 to 6 charges. The slag from the converter contains $1\frac{1}{2}$ to $2\frac{1}{2}$ % of copper and is re-smelted. Copper produced by this method is known as blister copper. (Fig. 137.)

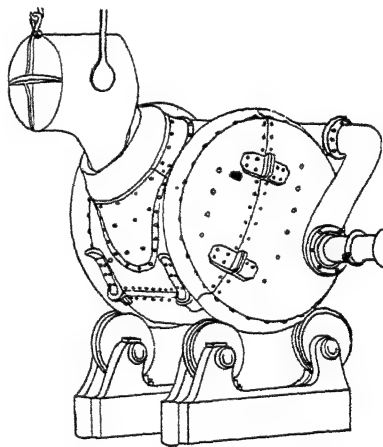


FIG. 136 Filling a Copper Converter.

468. Refining of Copper. Since copper prepared in this way is only about 98% pure it must be refined. This may be done by blowing compressed air into it to remove by oxidation small amounts of iron, sulphur and arsenic, but most of it contains enough gold and silver to make refining by electrolysis profitable. In this method thin sheets of electrolytic copper

having an area of about 6 square feet on each side form the cathodes and are arranged in parallel. The anodes are plates of cast copper from the converter with an area the same as the cathodes and arranged the same way. The electrolyte is copper sulphate and free sulphuric acid. Hydrochloric acid or salt is added to precipitate silver that might otherwise collect on the cathode with the copper. A current of 8 to 18 amperes per square foot of cathode surface is passed and the crude copper

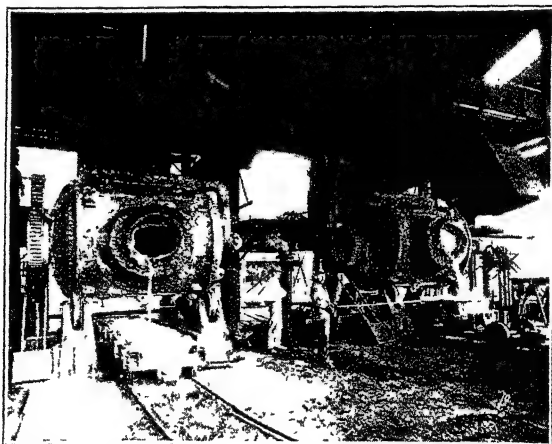


FIG 137. Emptying a Copper Converter.

dissolves and is deposited upon the cathode. The solution is kept at a nearly uniform temperature and is stirred from time to time to insure uniformity in composition. The gold and silver fall to the bottom with various impurities forming a slime which is removed at intervals and is refined by appropriate methods.

469. Physical Properties. Copper is a bright reddish colored metal. It is malleable, ductile, flexible, hard and tough,

and may be easily worked but does not yield good castings of large size. When rubbed with the hand it gives a disagreeable odor. It can be volatilized in the oxyhydrogen flame. It is an excellent conductor of heat and electricity, standing next to silver. Copper is second to iron in tenacity and stands third in malleability.

470. Chemical Properties. In dry air copper is unaltered, but it absorbs oxygen in the presence of water and carbon dioxide, forming a green hydrocarbonate of copper. At bright red heat it decomposes water.

Copper stands below hydrogen in the list of chemical activity, (see §36) so that no hydrogen is evolved when the metal is placed in dilute acids. Nitric acid reacts with copper according to the manner described in §135, forming the nitrate and nitrogen dioxide; hot sulphuric acid gives the sulphate and sulphur dioxide; boiling hydrochloric acid gives cuprous chloride and a slow evolution of hydrogen. When heated in the air to high temperatures it forms black copper oxide, CuO , if oxygen is in excess, otherwise it forms the red cuprous oxide, Cu_2O . At high temperatures copper colors the Bunsen flame green. Copper will replace such metals as mercury from solutions of their compounds, but is replaced by such metals as zinc, iron, magnesium, etc.

471. Uses of Copper. Copper is used for various pieces of laboratory apparatus, stills, retorts, beakers, etc., for kitchen utensils, for electric cables, dynamo and motor windings, as sheeting for the bottoms of ships and the roofs of houses, in coins, electrotypes and in many alloys and for copper plating.

COMPOUNDS OF COPPER

472. Copper Sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, commonly called blue vitriol or blue stone, may be made by treating copper with sulphuric acid, but if purity is not essential it is often made by roasting copper ore, and thus made will contain ferrous sulphate.

COPPER ALLOYS

<i>Alloy</i>	<i>Copper</i>	<i>Zinc</i>	<i>Tin</i>	<i>Other constituents</i>	<i>Uses, etc</i>
Brass	63-73	27-37			Typical brass Dutch metal Muntz metal and Pinchbeck are varieties of brass
Mosaic gold	65 00	35 00			
Gun metal	91 00		9 00		For ordnance
Bell metal	76 50		23 50		
Speculum metal	66 6		33 4		Mirrors and gratings for work in light; British coins
Bronze	95 0	1 0	4 0		
Phosphor bronze	82 25		12 95	Pb, 4 28; P, 0 52	
Phosphor bronze	79 7		10	Pb, 9.5 P, 0 8	
Manganese bronze	83 45			Mn, 13 48; Fe, 1 24; Co, 0 11,	Yellowish gray
Manganese bronze	81 03			Mn, 16.86; Fe, 1 67; Co, 0 06	Yellowish white
Silicon bronze	99 94		0 03	Fe, Si, trace	Telegraph wire
Silicon bronze	97 12	1 12	1 14	Fe, Si trace	Telephone wire
Bearing metal	79			Pb, 14; Sb, 6; P, 1 See also §500	

When heated to 240° copper sulphate loses its water of crystallization and becomes dehydrated copper sulphate, CuSO_4 , a white powder that becomes blue again if brought in contact with water. It therefore serves as a test for water and may be used as a dehydrating agent. Copper sulphate dissolves in four parts of cold, or in two parts of boiling water yielding a blue solution. With an excess of ammonia, copper sulphate forms copper ammonio sulphate, $\text{CuSO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$, which separates as dark

blue crystals when alcohol is added. Copper sulphate is used in medicine, in dyeing black on wool or cotton, as a preservative of wood, as an insecticide, in electrotyping and for electric batteries. It is poisonous and must not be tasted. Bordeaux mixture is made from 8 parts of copper sulphate solution with 8 parts of lime dissolved in 10 parts of water. It is used for spraying grape vines, etc.

473. Other Compounds. Copper forms two chlorides, *cuprous chloride*, CuCl , white crystals that are insoluble in water, and *cupric chloride*, CuCl_2 , blue-green crystals soluble in water and containing two molecules of water of crystallization. There are two sulphides, *cuprous sulphide*, Cu_2S and *cupric sulphide*, CuS , the latter being formed when hydrogen sulphide is passed into a solution of a copper salt or by fusing copper with sulphur. There are two oxides. *Cuprous oxide*, Cu_2O , occurs native or may be prepared as a bright red crystalline powder by boiling a solution of copper acetate with grape sugar. *Cupric oxide*, CuO , is a black solid formed by heating copper nitrate, or by heating copper in an excess of air to a high temperature. It may be reduced by hydrogen or carbon, and is therefore used in the laboratory for the analysis of organic substances and to determine the gravimetric composition of water. (Fig. 138.)

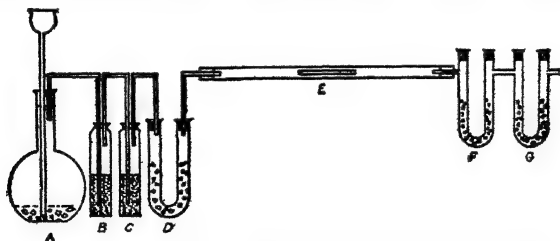


FIG 138. Reduction of Copper Oxide by Hydrogen.

Copper nitrate, $\text{Cu}(\text{NO}_3)_2$, is a blue crystalline solid formed by the action of nitric acid on copper. It contains 3 or 6 molecules of water of crystallization, is soluble in water and is decomposed by heat into cupric oxide and nitrogen oxides. Green verdigris is

copper subacetate $\text{CuO} \cdot \text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 6\text{H}_2\text{O}$ and is used in pigments, dyeing, etc. Verdigris varies in color and to some extent in composition.

The most delicate test for dissolved copper has been found to be that of Ohrmann-Spitzer which will detect 0.000000005% of copper. The reagent consists of 1.5 gram each of α -naphthol, paraphenylenediamine and sodium hydroxide dissolved in 100 cc. of distilled water. It is diluted from 1 to 100 before use. To 3 cc. of the solution to be tested add 0.5 cc. of the dilute reagent and heat to 100° . A red or violet color indicates copper.

SILVER

474. Occurrence. Silver has been used for money, ornaments, etc., for thousands of years. Much of it is now obtained as a by-product in lead or copper smelting, but it occurs free, or combined with sulphur; antimony and sulphur; arsenic and sulphur; copper, antimony and sulphur; or with chlorine as the more important ores.

475. Extraction of Silver. Several methods are used to extract the silver from its ores. Among these may be mentioned the Patio or amalgamation process where the ore, after being crushed, is mixed with salt which changes the silver to silver chloride, from which the metal may be extracted by amalgamating with mercury and distilling the amalgam, when the mercury passes off as a vapor and is condensed for further use. The loss of mercury is rather heavy since the process may require several weeks.

Another method depends upon the formation of a silver zinc alloy. The mixture of lead and silver is melted, zinc is added which combines with the silver and floats upon the lead. After skimming, the lead, mixed with the silver and zinc, is mostly pressed out and the zinc is removed by distillation. The silver, still containing a little lead is then melted in a bone-ash porous cupel. The lead is oxidized to litharge, and is driven off by

blasts of air or is absorbed by the cupel. The silver does not oxidize since it is covered by the litharge which at last bursts, exposing the silver as a bright liquid that is then removed.

476. Properties of Silver. Silver is a very brilliant white metal, very malleable and ductile, and is the best conductor of heat and electricity. In hardness it stands between gold and copper. It melts at about 961° , and when fused absorbs 22 times its volume of oxygen which is given off again when the metal cools, causing part of the metal to be projected from the vessel. At the temperature of the oxyhydrogen flame silver produces a green vapor. At ordinary temperatures silver is not acted upon by oxygen, the so-called oxidation or tarnishing of silver being due to the formation of the sulphide whenever silver comes in contact with compounds containing sulphur, such as eggs, mustard, perspiration, rubber bands, illuminating gas, etc. Ozone converts silver to the peroxide, Ag_2O . Hydrochloric acid acts slightly on silver, forming silver chloride that coats the silver, and thus prevents any further action. With sulphuric acid and nitric acid, reactions occur that are similar to those that occur when these acids act upon copper. Potassium hydroxide and sodium hydroxide do not attack silver which permits the use of silver dishes in making the two alkalies. "*Fine*" silver is 99.9% pure. It is usually expressed as 999 parts fine. *Sterling silver* is 925 parts silver and 75 parts baser metals for hardening. The baser metals are usually 70 parts copper and 5 parts cadmium. The cadmium gives soundness and malleability to the silver and removes the oxygen. It is added to the silver and copper after the two metals are melted and is pushed down beneath the mass to keep it from igniting. One formula for silver solder contains 55 to 65% silver, 20 to 30% of copper, 10 to 20% of zinc and about 3% of arsenic trioxide.

COMPOUNDS OF SILVER

477. Silver Nitrate, AgNO_3 , is formed by the action of nitric acid on silver or silver oxide. The crystals are colorless,

rhombic plates that do not change in the light unless organic matter touches them. If the finger is taken as an example of an organic compound and some silver nitrate is placed upon the finger, the nitrate is reduced and a black spot appears upon the finger. Silver nitrate is soluble in its own weight of cold water or in half its weight of boiling water, giving a neutral solution which will darken in the light if organic matter in the air comes in contact with it. It is, therefore, kept in brown bottles. It is used in indelible inks and is a valuable laboratory reagent. *Lunar caustic* is fused silver nitrate and is used to remove warts and other growths on the flesh. Silver nitrate gives a neutral solution which shows that although silver hydroxide is not known it is not a weak base, since nitric acid is a strong acid. The action of sodium or potassium hydroxide upon silver nitrate solution produces silver oxide instead of the hydroxide. When hydrochloric acid or a soluble chloride is added to silver nitrate or other soluble silver salt, *silver chloride*, AgCl , is formed. This appears as a white, curdy precipitate, that darkens on exposure to light, becoming violet or black owing to the presence of organic matter. It is insoluble in water. Silver chloride may be formed by the action of chlorine gas upon silver. The chloride melts at 460° and solidifies on cooling to gray, hornlike masses that may be cut with a knife. *Silver bromide*, AgBr , and *silver iodide*, AgI , are formed in ways similar to the formation of silver chloride. They are used in photography, their use depending on the fact that when mixed with organic matter and exposed to light they change color, and are reduced to metallic silver.

478. The Photographic Process. A thin layer of gelatin mixed with silver bromide is spread upon a glass plate or upon a thin film of celluloid which is exposed in the camera. The light given off by the photographed object begins to change the silver salt and this is continued when the plate is developed by an alkaline solution of pyrogalllic acid, ferrous sulphate, hydroquinone or other special reducing agents, of such slight activity that the action upon the non-exposed parts is practically none.

The image then appears as a negative—dark where the object was light and light where the object was dark. (Fig. 139.) The image on the plate is a deposit of finely divided silver and as the plate still contains silver salt not affected by the light this must be removed by washing with sodium thio-sulphate, usually called hyposulphite or "hypo," the process being known as fixing, otherwise the entire plate would be clouded and spoiled.

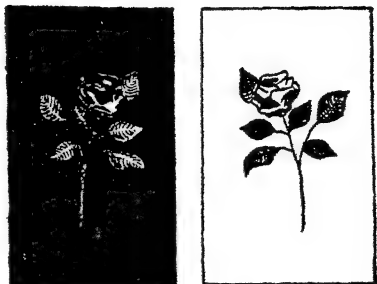


FIG. 139 Photography, Showing Negative and Positive.

An accelerator is sometimes used, and this is naturally alkaline in reaction, since the development is always carried on in an alkaline solution. The accelerators used are sodium hydroxide, potassium hydroxide, ammonium hydroxide, sodium carbonate, and potassium carbonate.

If the developer is too strong, causing it to act upon parts of the plate not exposed to the light, a restrainer is used. This action of the developer is known as "chemical fog," to distinguish it from "light fog." Since the developer is acting upon silver bromide, the use of a bromide as a restrainer is to be expected, and potassium bromide is usually used. Sodium bromide, ammonium bromide, and sometimes the citrate of the alkaline metals are also used. For the reduction of contrasts the alkali is increased, and the restrainer and reducing agent are reduced. For increase of contrasts increase the restrainer and reducing agent and reduce the alkali. To counteract over-exposure increase the bromide and reduce the alkali to a minimum. To make the best of under-exposure dilute freely, reduce the bromide to a minimum, or omit if possible, reduce the develop-

ing agent, and use as much alkali as possible without producing fog.

The picture is made by exposing a piece of sensitized paper to the light in such a manner that the light must pass through the plate or film before reaching the paper. The passage of the light is obstructed by the deposit of silver in proportion to the thickness of the metal and the picture thus becomes the negative of the negative, and receives the same shading as the object. The paper chosen should depend upon the negative and should print all that may be seen on the negative by transmitted light. A coarse paper scatters the lights and shadows, giving breadth of effect and atmosphere. It is not good for small pictures where clear definition, fine detail, and delicate gradations are desired. A hard paper is better to preserve the gradations of light and shade. Such papers as Platino, regular bromide and modified bromide are known as developing papers, from the fact that invisible and slightly visible images, the result of printing, are developed to full strength by developing agents. Velox and Dekko papers are gas light developing papers. Papers such as collodio-chloride, Aristo Jr., Aristo Platino, etc. are commonly called printing out papers, because the temporary image of partially reduced silver salts is printed to full strength, and afterwards partially replaced and wholly enveloped and protected by gold, producing tones of reddish black, brown-black, brown, sepia, etc. Further treatment with platinum produces tones of purple-black, olive brown, blue-black and black. The fixing agent for papers is sodium thiosulphate, the same as for the negative. When toned with gold or platinum the solutions used are gold chloride or chlorplatinic acid. Blue print paper is made by coating the paper with a solution of green scales of ferric ammonium citrate, $(\text{NH}_4)_2\text{HFe}(\text{C}_6\text{H}_3\text{O}_7)_2$, and potassium ferricyanide $\text{K}_3\text{Fe}(\text{CN})_6$. When the paper is used for making prints the parts exposed to the light turn dark blue while the unexposed portions do not change and when the paper is dipped into water the unchanged salts are washed out leaving white

lines. A recent French formula requires gelatin coated paper such as is used for the double-transfer carbon process and the solution contains ferric ammonium citrate (green scales) 15g. potassium ferricyanide 3.5g. in 100 g. of water.

479. Silver Plating is essentially the electrolysis of a silver salt by which the silver is deposited upon the object to be plated, while the strength of the solution is kept up by the slow dissolving of a piece of pure silver. The articles to be plated are first carefully cleaned and are then arranged in parallel to form the cathode. Pieces of pure silver arranged in parallel form the anode. The cathode and anode are placed in a bath of potassium silver cyanide, $KAg(CN)_2$, and the current from two or more cells arranged in series or from a dynamo is passed. The solution is decomposed and the silver is deposited upon the cathode or objects to be plated, while the pure silver slowly dissolves and thus keeps the strength of the solution constant.

The silvering of mirrors is accomplished by reducing silver nitrate by organic compounds, such as potassium sodium tartrate, glycerine, formaldehyde or sugar. On a small scale dilute silver nitrate is mixed with ammonium hydroxide until the solution is clear, then a little caustic potash, a few more drops of ammonia, and finally a very little glycerine are added. If a watch glass is floated in the mixture it soon acquires a deposit of silver.

480. Uses of Silver. In addition to the use of silver salts in photography and of silver in silver plating, the metal is used extensively for coinage and for ornamental or useful articles. For these purposes it is alloyed with copper to make it harder.

GOLD

481. Occurrence and Preparation. Gold occurs either free or combined, and the method of obtaining the metal depends upon the way in which it occurs. When free, that is, simply mixed with earth, sand or gravel, it may be separated by simply washing with water, the operation being conducted in long,

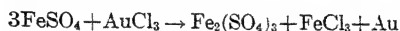
narrow boxes in which pockets are placed to catch the heavy gold while the lighter materials are carried away. (Fig. 140.) Mercury is sometimes placed in the pockets to amalgamate the



FIG 140. Placer Mining

gold. When the gold occurs as ore it is first broken into small pieces, crushed in a stamping machine until it has a diameter of one millimeter or less and is then carried out of the machine by water, and over plates of copper amalgamated with mercury. This will amalgamate the gold, while the quartz, pyrites, etc., are carried away. A little mercury is added at intervals to keep the proper consistency. About once a day the amalgam is scraped from the plates and strained through chamois skin or fine linen bags which retain the hard amalgam, while the unamalgamated mercury passes through and is used again. The hard amalgam is distilled from an iron retort, the mercury passing off as vapor and condensed under water while the gold and whatever silver is present remain in the retort. They are treated with borax, soda, potassium nitrate, etc., to remove baser metals.

The gold may be separated by dissolving the metals in aqua regia, forming gold chloride, AuCl_3 , evaporating the nitric acid, diluting and treating with a reducing agent, such as ferrous sulphate. The equation for such a reaction would be



482. In the Chlorination Process, which is used when the gold in the ore does not amalgamate readily, the ore is first roasted to change the sulphides, arsenides, etc., to oxides. It is then put into iron barrels lined with lead in which is some sulphuric acid. Bleaching powder is then added and the covers are fastened. The bleaching powder and the acid form chlorine which unites with the gold to form gold chloride. After revolving the barrel for $1\frac{1}{2}$ to 6 hours, the gold chloride is washed out with water, filtered and precipitated as gold sulphide, Au_2S , by means of hydrogen sulphide. The sulphide is filtered, then roasted in iron trays in a muffle furnace heated from above. This forms sulphur dioxide and free gold.

483. In the Cyanide Process, the ore is crushed, washed and treated with a weak solution of potassium cyanide forming a double cyanide of gold and potassium, $\text{KAu}(\text{CN})_2$, from which the gold is precipitated by zinc, or if not much gold is present, it may be separated by electrolysis. In nearly all cases gold ores contain silver and silver ores contain gold so that the two metals must be separated, the methods used depending upon the relative amounts of the two metals. The methods of separating may be divided into three classes. (1) Acid processes, where nitric acid, sulphuric acid or aqua regia is used. (2) The chlorine process, where the chlorine will combine with the silver at a lower temperature than it will with the gold. (3) Methods of electrolysis where the nature of the electrodes and the strength of the amperage differ according to the amount of gold present. If much gold is present the cathodes are gold, the electrolyte is a solution of gold chloride and free hydrochloric acid containing 40 to 45 grams of the chloride and 20 to 50 cubic centimeters of

the acid per liter, while the current gives 30 or more amperes per square foot of cathode surface. If the metal contains much silver and little gold the cathodes are pure silver, the electrolyte is a dilute solution of silver nitrate and nitric acid, while the amperage is about half as much as in the other case.

The purity of gold is expressed in carats or 24ths, pure gold being 24 carats fine, while 18 carat gold is 18/24 gold and the rest is copper or some other metal that will make the gold harder, since pure gold is too soft to resist the wear that accompanies constant use. During the first half of the nineteenth century the world's production of gold averaged 27 tons annually. The annual production is now about 500 tons of which about 30% comes from North America.

484. Properties. Gold, known as the "King of Metals," is a rather soft, yellow, malleable and ductile solid. It may be rolled into sheets so thin that over 250,000 of them are required to make a pile one inch high. By transmitted light these thin sheets appear green, while by light reflected 10 times from gold surfaces, the metal appears bright red. Gold melts at about 1063° and volatilizes at higher temperatures giving a green vapor. It combines directly with chlorine, but not with oxygen. The common acids taken singly, either cold or hot will not react with pure gold because it is so inactive chemically, (see §36) but aqua regia reacts with it, forming gold chloride. Caustic alkalies act upon gold.

485. Uses of Gold. Gold hardened by the addition of some copper is used for coinage and has a reddish color; alloyed with copper or silver it is used for gold plate or for ornaments. Gold used for jewelry is usually from 10 to 22 carats fine. Gold leaf is used for lettering, etc., and baser metals as silver or copper are frequently plated with gold. The method of gold plating is about the same as for silver plating, except that the anode is gold and the bath is a solution of 1 part of gold cyanide, $\text{Au}(\text{CN})_3$, and 10 parts of potassium cyanide in 100 parts of water. The alloys containing gold are shown in the following table:

ALLOYS FOR COINAGE

<i>Coin</i>	<i>Gold</i>	<i>Silver</i>	<i>Copper</i>	<i>Other constituents</i>	<i>Where used</i>
Gold	91 66		8 33		Great Britain
Gold	90 00		10 00		United States
Silver		92 5	7 5		Great Britain (Sterling Silver)
Silver		90 0	10 0		United States
Nickel			75 00	Ni 25 00	United States
Copper			95 0	Sn 3 0; Zn 2 0	United States

486. Compounds of Gold. Gold forms a number of compounds, the best known being gold chloride, AuCl_3 , formed when aqua regia acts upon gold. The presence of gold in gold chloride may be detected by adding some stannous chloride solution, SnCl_2 , which gives a purple colored precipitate, known as the purple of Cassius, which is said to be very finely divided gold. The other compounds are not very important in elementary work and are not used to any extent on account of their cost.

PLATINUM

487. Occurrence and Preparation. Platinum ore always contains one or more of the following metals: Iridium, osmium, ruthenium, rhodium, palladium, gold, silver, iron, copper, nickel, etc. It also occurs as sperrylite, PtAs_2 . The ore usually contains 60 to 80% of platinum which must be separated from the other metals. The ore is washed and the gold is separated by amalgamation. The ore is then treated with dilute aqua regia to remove any remaining gold, the silver and copper. The solution is evaporated and heated to 125° , which changes the iridium and palladium to the sesquichlorides. It is then dissolved in hydrochloric acid or in concentrated aqua regia, which changes the platinum and a little of the iridium to soluble compounds. Ammonium chloride is then added and the platinum is precipitated as ammonium platinic chloride, $(\text{NH}_4)_2\text{PtCl}_6$, which decomposes when strongly heated into ammonium

chloride, chlorine and spongy platinum. The spongy mass is melted in a lime crucible by means of an oxyhydrogen flame and is hammered or rolled while hot into bars and sheets. It usually contains a little iridium which is not removed unless the platinum is to be absolutely pure. The other metals that occur with platinum have very limited uses, one alloy of iridium and osmium being used for the tips of gold pens. Platinum was first taken to Europe from South America in 1735. The present supply is found chiefly in Russia. The price has increased 500% during the past 15 years.

Platinum is found in Canada to the amount of less than 100 ounces per year. But it has been estimated that probably more than 50,000 ounces are lost in ores mined each year owing to imperfect methods of recovery, indicating that Canada may become one of the largest producers of the metals of the platinum group.

488. Properties. Platinum has a grayish white color, and resembles polished steel. It is very malleable and ductile and at white heat can be welded like iron. Its specific gravity varies from 21.1 to 21.5 according to the method of treatment. It does not react with nitric, hydrochloric or sulphuric acid, but reacts with aqua regia, forming chlorplatinic acid, H_2PtCl_6 . Some of the alkalies act upon it, such as a mixture of potassium nitrate and potassium hydroxide. It reacts with red hot charcoal and silicon dioxide, forming a compound of silicon and platinum. When platinum is in a finely divided condition it has the curious property of absorbing certain gases, and the gases thus absorbed are very active chemically. In this way 200 volumes of oxygen are absorbed by platinum, and the oxygen is capable of oxidizing other substances when brought in contact with it. Advantage is taken of this fact in the manufacture of sulphuric acid by the contact process. (§298.)

A current of hydrogen is lighted when it flows against a platinum sponge, owing to the oxygen that is in the pores of the sponge and the amount of heat generated. When platinum

exists as a black porous mass it is known as spongy platinum, and still finer platinum is called platinum black. It forms alloys with lead and with the metals with which it is found in nature, and these should never be heated in platinum dishes.

489. Uses of Platinum. Platinum is used extensively in all chemical laboratories as wire, foil, crucibles, evaporating dishes, etc. Platinum apparatus is very expensive, owing to the scarcity of the metal and the great demand for it.

Its coefficient of expansion is about the same as that of glass so that the wire may be fused into the glass without cracking the glass when cold. On account of this property and from the fact that it is a good conductor of electricity, it was formerly used in electric light bulbs where it conducted the current from the external wires to the internal carbon filament, but at present nickel steel wire covered with copper is used. With 10% of iridium it forms a hard alloy and is used for international meter sticks. The alloy is hard, elastic, fuses with difficulty and is unchanged by contact with air.

Platinum is replacing gold to some extent in jewelry, but its use should be discouraged, because of more vital uses for platinum in sciences. A substitute for platinum for electrical contacts consists of platinum, 45%; gold, 15%; silver, 25%; and copper, 15%. Tungsten is also being used extensively.

Owing to the scarcity, high cost and great demand many substitutes for the metal are on the market. Some of these are shown in the table.

<i>Sample</i>	<i>Au</i>	<i>Ag</i>	<i>Pd</i>	<i>Cu</i>	<i>Ni</i>	<i>Zn</i>	<i>Pt</i>
1*	45	45	10				
2**	90			10			
3***	75-85				10-18	2-9	
4	15	25		15			45

*Rh or Ir may be substituted for the silver. Used for sparking terminals.

**Used as cathodes. May be used as anodes if electrically coated with Pt.

***Used as "white gold" as a substitute for Pt in jewelry.

W, Au, Ni; Ag, W, Ni; Ni, Fe=Platinite; NiCr; CoFe; CoCr alloys.

Palau	}	Good for cathodes but not for anodes.
Rhotanum		

PLATINUM COMPOUNDS

490. Platinic Chloride, $PtCl_4$, is the most important compound of platinum. It is formed by dissolving platinum in aqua regia and evaporating the solution to dryness when a brownish solid is obtained, soluble in water or in alcohol to a golden yellow solution, used in qualitative analysis and in the preparation of platinum prints.

Chlorplatinic Acid, H_2PtCl_6 , formed by dissolving platinic chloride in hydrochloric acid, yields chlorplatinate or double chlorides, such as potassium platinic chloride, K_2PtCl_6 , ammonium platinic chloride, $(NH_4)_2PtCl_6$, both difficultly soluble in water and, therefore, easily obtained as yellow crystals when platinic chloride solution is added to a solution of potassium chloride or ammonium chloride.

491. Problems.

1. How much copper sulphide can be formed by heating sulphur with 20 grams of copper?
2. At 50 cents per ounce what is the value of the silver set free from five kilograms of silver chloride by iron?
3. How much silver chloride will be formed by adding sodium chloride to five grams of silver nitrate in solution? (§185).
4. How much gold will 10 grams of ferrous sulphate liberate from a solution of gold chloride according to the equation given in §481?
5. How much sulphuric acid will react with a plate of copper 12 centimeters long, eight centimeters wide and two centimeters thick if the specific gravity of copper is 8.9?
6. How much potassium platinic chloride is formed when five grams of platinic chloride react with potassium chloride?
7. How much ammonium platinic chloride is formed when 10 grams of ammonium chloride react with platinic chloride in excess?
8. How many grams of nitric acid will be required to react with the copper that is formed by the reduction of 10 grams of copper oxide, CuO , by hydrogen? How much hydrogen is required to reduce the oxide? How many grams of zinc and how many cubic centimeters of sulphuric acid (specific gravity 1.84) are required to supply the hydrogen?

CHAPTER XXII

MAGNESIUM, ZINC, CADMIUM AND MERCURY

492. Comparison of the Metals of this chapter.

<i>Metal</i>	<i>At. Wgt</i>	<i>Valence</i>	<i>Specific Gravity</i>	<i>Melts</i>	<i>Boils</i>
Mg	24 32	2	1 741	651°	1100°
Zn	65 37	2	6.48-7.2	419°	918°
Cd	112 4	2	8 37- 8 67	321°	778°
Hg	200 6	1,2	13 54-14 4	-38 7°	357 25°

MAGNESIUM

493. Occurrence and Preparation. Magnesium is produced chiefly by the electrolysis of fused carnallite, a double chloride of potassium and magnesium, $\text{KCl} \cdot \text{MgCl}_2$. Since the carnallite contains 6 molecules of water of crystallization it must first be fused to drive off the water.

Calcium fluoride or sodium chloride is added as a flux and the operation is conducted in a closed iron crucible, which is made the cathode, while a carbon rod serves as the anode. The anode is enclosed in a perforated porcelain cylinder with a tube at the top for the removal of the chlorine. The magnesium floats upon the melted carnallite and is kept from oxidizing by an inert gas, such as hydrogen, which is admitted to the crucible.

Magnesium may also be obtained by the electrolysis of a fused mixture of 55 parts of magnesium fluoride, 5 parts of sodium fluoride and 40 parts of barium fluoride. The temperature of electrolysis is 900-1000° and the current density at the cathode is 400 amperes per square foot. The cell consists of a cast iron container, cooled at the base and encrusted with solid electrolyte. The cathode or cathodes are of iron, with points projecting through the base. The anodes are of carbon. Above

the cathode is a cooling coil which produces a crust sufficient to protect the floating magnesium from the air but easily broken when the metal is to be removed. On the electrolyte floats a layer of MgO or MgCO_3 , part of the oxide becoming suspended and combining with the fluorine set free. This layer also protects the anodes.

Magnesium occurs also in asbestos, MgCaSiO_3 ; in talc, $\text{N}_2\text{Mg}_3\text{Si}_4\text{O}_{12}$; in dolomite, magnesite, meerschaum, olivene, etc.

494. Properties and Uses. Magnesium melts at 651° , becomes volatile at higher temperatures, and at ordinary temperatures decomposes water very slowly. The color of the metal is silver white or grayish and it has a high luster. It is tenacious and ductile and is drawn into wire or rolled into ribbon. It does not change rapidly in the air, but is gradually covered with a layer of the oxide or the hydroxide. Magnesium burns with a white light, especially in oxygen, forming white magnesium oxide, and if burned in air, some magnesium nitride is formed. Powdered magnesium is used to produce the light for flashlight photographs. The light from burning magnesium will explode a mixture of hydrogen and chlorine. Magnesium combines directly with nitrogen at high temperatures and forms magnesium nitride, Mg_3N_2 , with the oxide, MgO , if the metal is burned in air.

MAGNESIUM COMPOUNDS

495. Magnesium Oxide, MgO , formed by burning magnesium metal, or by heating basic magnesium carbonate, is a white powder called magnesia. Since magnesium is such a light metal the combination with oxygen gives an increase of $66\frac{2}{3}\%$ in the weight. Magnesium oxide does not dissolve in water, but unites with it forming magnesium hydroxide, $\text{Mg}(\text{OH})_2$, which is feebly alkaline in its reactions. Magnesium oxide is practically infusible and is used for lining crucibles, furnaces, etc., where high temperatures are required. It is used in medicine as an antidote for mineral acids. Mixed with

water and sand magnesium oxide becomes very hard and is used as a cement. Magnesium oxide or hydroxide mixed with magnesium chloride and water gives a basic chloride of varying composition which becomes very hard and may be used as a cement or plaster. Magnesium oxide and wood pulp are used as artificial stone.

496. Magnesium Sulphate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, commonly called Epsom salts, is a white crystalline solid containing seven molecules of water of crystallization, six of which pass off readily, but the seventh is driven off at temperatures above 200° so that the last molecule of water is often called water of constitution. The sulphate is soluble, one part of water dissolving one and one-fourth parts of the salt. It is used as a fertilizer, in the manufacture of sodium sulphate and potassium sulphate, to load cottonfabrics, and in medicine. In British Columbia are 5 lake-beds with a total area of 20 acres containing hydrated magnesium sulphate, the salt beds being in some places 40 feet deep and averaging 73.04 to 91.28% Epsom salt. Some of the surface deposits are practically chemically pure.

497. Other Magnesium Compounds. *Magnesium carbonate*, MgCO_3 , occurs in nature as magnesite or combined with calcium carbonate as dolomite. *Magnesia alba* is a complex mixture of the carbonate and the hydroxide and is used for face powders.

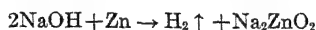
Magnesium chloride, MgCl_2 , is a white solid, which will crystallize with six molecules of water of crystallization. It is very deliquescent and is sometimes present in sodium chloride, causing it to become damp. Several other salts and double salts of magnesium are known.

ZINC

498. Preparation. Zinc does not occur free, but is found chiefly as blende, ZnS , smithsonite, ZnCO_3 , and hemimorphite, $\text{Zn}_2\text{SiO}_4 \cdot \text{H}_2\text{O}$, although it occurs also in other combinations as zinc oxide, etc. Blende is first roasted to get rid of the sulphur;

the others are often calcined to get rid of the carbon dioxide and water. The pulverized ore is mixed intimately with anthracite coal or with coke and soft coal, and is placed in clay retorts which are placed in the furnace in a nearly horizontal position. The mixture is heated and the vapors are condensed in receivers of clay or iron surrounded by air. The first part of the condensation is zinc dust containing zinc oxide, but after the temperature is raised to nearly 1300° , the oxide is decomposed and metallic zinc in the form of a liquid collects and is cast into plates. This always contains impurities such as iron, arsenic, carbon, lead, cadmium, etc., but the metal may be obtained in a pure state by repeated distillations.

499. Properties. The color of zinc is bluish white and the metal has a high luster when perfectly pure. Its specific gravity varies from 6.48 to 7.2, depending upon whether it is melted or rolled. At ordinary temperatures zinc is brittle; between 100° and 150° it can be rolled into sheets; above 200° it again becomes brittle. The surface of zinc in moist air soon tarnishes, but in dry air it does not change. When heated to its melting point zinc burns with a bluish or greenish flame, forming white zinc oxide, ZnO , formerly called philosophers' wool or flowers of zinc. With the common acids zinc acts as a base forming element, displacing the hydrogen and forming a zinc salt. With nitric acid the hydrogen reacts with the acid, forming ammonium nitrate. If the zinc is pure, the reaction with sulphuric acid is slow but may be hurried by adding copper sulphate solution. With caustic alkalies zinc acts as an acid forming element liberating hydrogen and forming the zincate of sodium or potassium, as



Zinc replaces lead and mercury from solutions of the salts of those metals.

500. Uses of Zinc. Zinc is used to make galvanized iron, which is a piece of sheet iron covered with a layer of zinc. It is used in batteries, (§199 ff.) and in several alloys.

ZINC ALLOYS

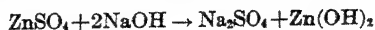
<i>Alloy</i>	<i>Zinc</i>	<i>Tin</i>	<i>Copper</i>	<i>Other Constituents</i>	<i>Uses, etc</i>
Antifriction metal	85 0		5 0	Sb 10 0	For bearings
Babbitt's metal	69 0	19 0	4 0	Sb3 0; Pb5 0	

Sherardized iron is produced by covering the article with zinc dust and baking. It is used to give a protective coating to screws, etc. The process of sherardizing is as follows: the objects to be coated are placed in an iron drum filled with zinc and zinc oxide and are heated in a reducing or inert atmosphere. Several coatings are produced upon the iron the one nearest the iron being an alloy rich in iron, upon which is a coating containing more zinc. This is followed by a coating containing a number of more or less unknown alloys and the final coat is a layer of pure zinc. In the Schoop process the zinc is melted and by the use of a special compressed air gun the melted zinc is atomized and applied to the surface to be covered. The process is also used to apply solder to metallic surfaces and is said to be very satisfactory.

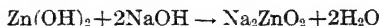
COMPOUNDS OF ZINC

501. Zinc Oxide, ZnO , as found in nature is red, owing to presence of manganese, but as prepared it is white. It turns yellow when heated. It is infusible, is not reduced by heat, is not soluble in water and is used as a substitute for white lead in paints. The value of zinc oxide in white paints depends largely upon the fact that if hydrogen sulphide acts upon the paint the sulphide of zinc is white while the sulphide of lead is black, the latter causing a gradual darkening of the paint.

502. Zinc Hydroxide is a white amorphous powder. It may be produced by adding sodium or potassium hydroxide to a solution of a zinc salt, such as the sulphate.



The hydroxide reacts with an excess of the alkaline hydroxide forming soluble sodium zincate, Na_2ZnO_2 ,



the same compound as when zinc is boiled with sodium or potassium hydroxide.

503. Zinc Chloride, ZnCl_2 , is formed when chlorine or hydrochloric acid acts upon zinc. It is a white solid containing one molecule of water of crystallization which it loses when strongly heated. It melts at 365° and forms an anhydrous mass on cooling which deliquesces in the air. It is very soluble in water. It is used in soldering, as a disinfectant, as a preservative of such materials as railroad ties and as a constituent of preparations used to fill teeth, etc.

504. Zinc Sulphide, ZnS , occurs in nature as blende containing iron and cadmium sulphides, and is yellow, brown or black in color. Zinc sulphide is partially precipitated when hydrogen sulphide is passed into a solution of a zinc salt of a strong acid, such as sulphuric, unless a soluble acetate is added. With zinc acetate precipitation is complete. When pure, zinc sulphide is white and is used as a pigment. Highly phosphorescent zinc sulphide is used for making the hands and figures on a watch visible in the dark. (See §532.)

505. Zinc Sulphate, ZnSO_4 , or white vitriol, is formed by the action of zinc upon sulphuric acid or by the oxidation of zinc sulphide. It contains seven molecules of water of crystallization of which six are easily lost when the sulphate is heated, the water then dissolving the salt, while the seventh is lost only at a temperature of 238° . At red heat zinc sulphate decomposes into zinc oxide, sulphur dioxide and oxygen. It is soluble, 100 parts of water dissolving 48.4 parts of the sulphate at 10° and 78.5 parts at 100° . It is used in cotton printing and dyeing, as a disinfectant and in medicine.

CADMIUM

506. Cadmium is obtained as a by-product when zinc ores are reduced. It sometimes forms 4 or 5% of the ores. As it is more volatile than zinc, it passes out first with the zinc dust as a brownish powder. This is collected and distilled once or twice for purification. The metal is silver white, and is harder than tin. Acids act with it readily. It is used in fusible alloys and in dental amalgam. Its compounds are not very important, the best known being *cadmium sulphide*, CdS , a yellow substance precipitated when hydrogen sulphide is run into a solution of a cadmium salt. It is used in yellow paint. Some of the other salts are the cyanide, sulphate, chloride, oxide and iodide, none of which need be described.

MERCURY

507. Occurrence. Mercury is sometimes found free in small quantities, but the most of it is derived from the native sulphide, HgS , called cinnabar, and found chiefly in Europe, Mexico, California and Texas. The metal is commonly called quicksilver. It has been known from the earliest times.

508. Preparation. Mercury is prepared by heating the sulphide in furnaces in contact with air which oxidizes the sulphur and sets the mercury free as impure vapor, which passes into chambers where it is condensed. (Fig. 141.) It is next

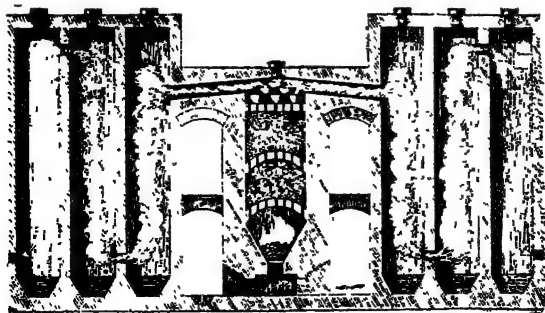
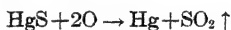


FIG. 141. Extraction of Mercury.

squeezed through chamois skin or linen bags to free it from dirt and is then redistilled to free it from such metals as lead, zinc, etc. About 1000 tons are produced annually in the United States and it is sold in strong iron cylinders holding 75 pounds net. Mercury is purified in the laboratory by washing with sulphuric acid, sodium hydroxide and water, separately. When the mercury ores are reduced in a furnace the general equation for the reaction may be written,



the sulphur being oxidized by the oxygen of the air. If the reduction occurs in a tightly sealed iron retort, lime or iron is generally added and the reduction occurs as in the following equations:



or



The retort method is used with only very rich ores.

509. Properties. Mercury is silvery white in color and is the only metallic element that is liquid at ordinary temperatures. It becomes solid at -39.5° and boils at about 357° , being converted into a colorless vapor with a density of 6.976 (air=1). Liquid mercury has a specific gravity of 13.5959 at 0° and when solid at -188° the specific gravity is 14.4. It is unaltered in the air except when sulphur compounds are present. At moderately high temperatures it combines slowly with oxygen forming red mercuric oxide, HgO . The molecule of mercury, like that of zinc and cadmium, probably contains only one atom instead of two atoms, as in the case of the elementary gases as oxygen, hydrogen, etc. Mercury is below hydrogen in the list of activity and therefore does not react with dilute hydrochloric and sulphuric acids when cold, but reacts with hot sulphuric acid, or with nitric acid, the latter acid giving mercurous nitrate, HgNO_3 , if the acid is dilute and cold but mercuric

nitrate, $\text{Hg}(\text{NO}_3)_2$, if the acid is concentrated and hot. Mercury combines with chlorine, bromine and iodine at ordinary temperatures and with sulphur at gentle heat.

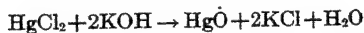
510. Uses of Mercury. Mercury is used in making thermometers, barometers, mercury air pumps and in extracting gold and silver. Its compounds are used in medicine and as disinfectants. When amalgamated with zinc it is used in batteries. It amalgamates easily with gold, silver or copper either when these metals are pure or when they are alloyed as in jewelry, so that the metal should never be allowed to come in contact with rings, watches, etc. Both mercury and mercury vapor are poisonous and care should be used not to inhale the vapors nor should mercury be placed in the mouth.

Recent experiments on the use of mercury vapor in boilers, in place of steam, showed 1,050 kilowatts of power delivered by the mercury boiler as compared with about 200 delivered by a steam boiler operating under similar conditions.

COMPOUNDS OF MERCURY

Mercury forms two classes of compounds, mercuric where the metal is bivalent, and mercurous where it is univalent. All common mercury salts are volatile and the vapors are poisonous.

511. Mercuric Oxide, HgO , is a dark, orange red powder when prepared by dry methods such as heating mercury or mercuric nitrate; but is a yellow precipitate when formed in wet ways, such as decomposing mercuric chloride by potassium hydroxide.

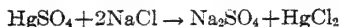


Mercuric oxide oxidizes sulphur, carbon and phosphorus energetically when heated.

512. Chlorides. *Mercurous chloride*, HgCl , or calomel, is a whitish semitransparent mass, insoluble in water. It is prepared by heating mercuric chloride with mercury and has a specific gravity of 7.10. It melts and volatilizes at the same

temperature, decomposing into mercuric chloride and mercury. It is used in medicine and when exposed to the light slowly changes to mercuric chloride, a violent poison. It must be kept, therefore, in colored bottles away from the light.

Mercuric chloride, HgCl_2 , may be formed by heating mercuric sulphate and sodium chloride, the equation for the reaction being written



or by the action of chlorine upon mercury; or by dissolving mercury in aqua regia, evaporating to dryness and subliming the residue. It is a white crystalline solid having a specific gravity of 5.4, melting at 288° and boiling at about 295° , giving a vapor that has a density of 9.42 (air = 1). It dissolves in 19 parts of cold water and the solution produces a white precipitate in the solution of the white of an egg, which is, therefore, the best antidote if the poison is swallowed provided absorption has not occurred. It is a very powerful antiseptic, a dilute solution containing one part of the chloride in 1000 to 8000 parts of water being strong enough for most purposes where it is used. Its use in surgery for washing wounds, instruments, etc. is universal. It is used as a preservative of wood, skins, etc.

513. There are *two iodides of mercury*, *mercurous iodide*, HgI , an unstable, yellowish green powder formed by the action of mercury on iodine or mercuric iodide; or by adding potassium iodide to a solution of a mercurous salt; and *mercuric iodide*, HgI_2 , a scarlet red powder formed by the action of mercury on iodine or by the action of potassium iodide on a solution of a mercuric salt.

The formation of mercurous and mercuric nitrates was described under chemical properties of mercury.

514. The Sulphates are formed in a similar manner. *Mercurous sulphate*, Hg_2SO_4 , is formed when equal parts of mercury and sulphuric acid are heated until $\frac{2}{3}$ of the mercury disappears. *Mercuric sulphate*, HgSO_4 , is formed when two parts of mercury

are heated with three parts of sulphuric acid and evaporated to dryness. Mercurous sulphate is a white crystalline powder slightly soluble in water. Mercuric sulphate is a white amorphous powder slightly soluble in water, and converted by water into a basic sulphate.

515. Mercuric Sulphide, HgS , is a native mineral known as cinnabar. It is red and crystalline. When hydrogen sulphide is passed into a solution of a mercuric salt, black mercuric sulphide is formed, but this turns red when heated. Vermilion is an artificial mercuric sulphide used in red paint, and to color sealing wax. It is made by grinding mercury and sulphur together for several hours in a mortar and washing with potassium hydroxide solution, or by heating mercury and sulphur in iron pans and subliming the black mass that is formed. This is washed with hot water and dried.

516. Problems.

1. How much magnesium must be burned to yield the magnesium oxide that will react with water to form two grams of magnesium hydroxide? (§495)

2. How much hydrogen will be freed and how much sodium zincate will be formed by the action of 10 grams of zinc upon sodium hydroxide? (§499).

3. How many cubic centimeters of sulphuric acid, (specific gravity 1.84) will react with a piece of zinc, (specific gravity 7.2) measuring $2 \times 5 \times 6$ centimeters?

4. How much mercuric oxide will be formed by the action of potassium hydroxide on 6 kilograms of mercuric chloride? (§511).

5. How much mercuric chloride can be formed by heating 35 grams of mercuric sulphate with salt? (§512).

6. Write quantitative equations showing the reaction between aluminum and potassium hydroxide, aluminum and sodium hydroxide, zinc and potassium hydroxide, zinc and sodium hydroxide. (§§441, 499).

CHAPTER XXIII

CHROMIUM, MANGANESE AND RADIUM

517. Comparison of the Metals of this Chapter.

<i>Metal</i>	<i>At. Wgt.</i>	<i>Valence</i>	<i>Specific Gravity</i>	<i>Melts</i>
Cr	52.0	2, 3, 6, 7	6.92	1520°
Mn	54.93	2, 3, 4, 6, 7	7.4-8	1260°
Ra	226.0	2	—	—

CHROMIUM

518. Occurrence and Preparation. Chromium occurs only in compounds and is not widely distributed in large amounts, the principal deposits occurring in Greece, New Caledonia, Canada and New South Wales, where the ore is found chiefly as chromite, FeCr_2O_4 , while native lead chromate, PbCrO_4 , occurs in smaller amounts and in some other localities, the annual production of the ores being about 30,000 tons.

Preparation. Chromium is prepared by Goldschmidt's thermit process, by igniting a mixture of chromic oxide, Cr_2O_3 , and aluminum. (See §442.)

519. Properties and Uses. Chromium is a brilliant grayish metal, the polished surface being whiter than iron. It is hard, non-magnetic and is unaltered in air. It melts at the temperature of the electrical furnace. At high temperatures it combines with oxygen, sulphur, carbon, silicon and boron. It reacts with hydrochloric and sulphuric acids, but is unaffected by nitric acid. It is used chiefly to make a hard steel known as chrome steel, (see §421) while ferrochrome contains 65 to 80% chromium and 20 to 35% of iron with a small amount of carbon.

Chromium alloys are being used for flat-irons since the wires made from them offer high resistance, melting at high tempera-

tures and hence can stand high heating without injury. One formula contains chromium 30 to 60%, copper 30 to 60%, tungsten 2 to 5% and molybdenum 1 to 3%. Another shows chromium 93 to 95%, tungsten 2 to 6% and aluminum 0.25 to 1%. The melting point is from 1200° to 1300°. Other chromium alloys are used for making acid resisting vessels. One formula shows chromium 60%, silicon 2 to 4%, graphitic carbon 2 to 5% and the rest iron. Another shows chromium 40%, molybdenum 3%, iron 55.5%, carbon 1.5%. See also cobalt alloys.

COMPOUNDS OF CHROMIUM

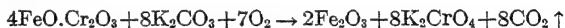
520. Chromium compounds may be divided into three classes according to the valence of the metal, since it usually acts as a bivalent, trivalent and hexivalent. Where the metal acts as a bivalent the compounds are called chromous, such as chromous oxide, CrO , chromous chloride, CrCl_2 . When the metal is trivalent the compounds are chromic, as chromic oxide, Cr_2O_3 , chromic chloride, CrCl_3 , chromic sulphate, $\text{Cr}_2(\text{SO}_4)_3$, etc. The chromates and dichromates are derived from chromium trioxide, CrO_3 , where the metal is hexivalent as in potassium chromate, K_2CrO_4 and potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$. When chromium has a valence of 2 it acts as an unstable base former, which upon exposure changes to a valence of 3, acting as a weaker base former, but producing more stable salts, green or purple in color. By oxidation the valence is increased to 6, when the chromium acts as an acid former, as in potassium chromate, and dichromate, which, like the other chromates, have a yellow or a red color. By further oxidation the perchromic compounds are formed, where the chromium has a valence of 7.

Chromium acts as a base forming element in the oxides, chlorides, and sulphates.

521. Chromic Oxide, Cr_2O_3 , is a green powder prepared by calcining mercurous chromate or by heating potassium dichromate with sulphur forming the oxide and potassium sulphate,

the latter being dissolved out with water. *Chromium trioxide*, CrO_3 , is formed by adding to a cold saturated solution of potassium dichromate, $1\frac{1}{2}$ times its volume of sulphuric acid. Dark red needle shaped crystals separate and should be drained and recrystallized in a small amount of warm water. This oxide is commonly called chromic acid or chromic anhydride corresponding to sulphur trioxide, and forming theoretically the unknown acid, H_2CrO_4 , from which are derived the chromates among which the most important are potassium chromate and lead chromate.

522. Chromates. Potassium chromate, K_2CrO_4 , is made by roasting chrome iron ore with potassium carbonate in a reverberatory furnace.



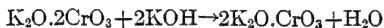
It is a lemon yellow solid, crystallizing in right rhombic prisms. It is very soluble in water giving a yellow solution even when 1 part is dissolved in 40,000 parts of water. When nitric or sulphuric acid is added it is changed to the dichromate, by neutralizing part of the K_2O .



Lead chromate, PbCrO_4 is formed when a soluble lead salt is treated with potassium chromate or potassium dichromate. It is a yellow solid, and is sold as a pigment known as chrome yellow. When treated with potassium hydroxide or sodium hydroxide in quantities not sufficient to dissolve it, lead chromate is changed to a red color known as chrome red, Pb_2CrO_5 . Among the other chromates may be mentioned those of barium, silver, sodium, etc.

523. Dichromates. If two molecules of the hypothetical acid, H_2CrO_4 , could be deprived of one molecule of water, a second hypothetical acid called dichromic acid, $\text{H}_2\text{Cr}_2\text{O}_7$, would be formed from which are derived the dichromates by replacing the hydrogen with a metal. The most important dichromate is

Potassium dichromate, $K_2Cr_2O_7$, formed when two parts of chromite are heated to redness with one part of potassium nitrate, or by the action of sulphuric acid on potassium chromate. Orange red crystals are formed dissolving in 8 to 10 parts of cold water and in a much smaller quantity of boiling water. It is decomposed by heat into potassium chromate, chromium trioxide and oxygen; or by potassium hydroxide into the chromate and water. When mixed with organic substances it is reduced on exposure to light; gelatin, under such circumstances is rendered insoluble. The reason for such a reaction may be readily seen when we write the formula for potassium chromate $K_2O.CrO_3$ and for potassium dichromate $K_2O.2CrO_3$. The potassium oxide (hydroxide in solution) is present in larger proportion in the chromate. Hence a solution of potassium hydroxide must be added to a solution of potassium dichromate to form the chromate

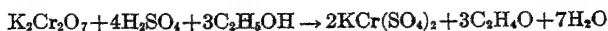


Potassium dichromate is an energetic oxidizing agent and is used in dyeing, bleaching, tanning, etc. In tanning it is used in place of tan bark, for kid glove leather, and reduces the time from 8 months or more to a few hours. A reducing agent is added to precipitate chromium hydroxide, $Cr(OH)_3$, in the leather. (See Chap. 36.)

With hydrochloric acid the following action occurs, the acid being oxidized to water while chlorine is set free and the chlorides of chromium and potassium are formed



Potassium dichromate will quickly oxidize any oxidizable material with which it comes in contact. With alcohol and sulphuric acid, potassium chromium sulphate, aldehyde and water are formed according to the following equation:



Potassium dichromate and sodium dichromate are the most important and best known of the dichromates. Very few others are formed since the chromate is precipitated as a general thing when either the chromate or dichromate of potassium or sodium is added to salt solutions.

MANGANESE

524. Manganese Forms Compounds Analogous to Chromium Compounds. Manganous salts are formed where the metal acts as a bivalent as manganous chloride, MnCl_2 , manganous sulphate, MnSO_4 , manganous hydroxide, Mn(OH)_2 , etc.

Here the metal acts as a base former. The salts are pink and relatively stable.

Manganic salts are formed when the metal acts as a trivalent, as manganic hydroxide, Mn(OH)_3 , manganic sulphate, $\text{Mn}_2(\text{SO}_4)_3$, manganic oxide, Mn_2O_3 , etc., where the metal acts as a weaker base former than where it is bivalent. When the valence is 4 the metal is a very weak base former and the manganese may act as either a base or an acid former.

Corresponding to chromic acid is manganic acid, giving manganates, H_2MnO_4 where the metal has a valence of 6 and acts as an acid former in a few unimportant compounds, while in permanganic acid, HMnO_4 , giving permanganates, the manganese acts as a strong acid former, with a valence of 7.

There is an oxide known for each of the series, and one, Mn_3O_4 , is thought to be a mixture of two others. In general the manganous salts and those of permanganic acid are more easily formed than the manganic salts and those of manganic acid thus differing from chromium which preferably forms chromic salts and those of chromic acid. Manganates are stable only in the presence of alkalis. When acidified they change to the permanganates and the color changes from green to purple.

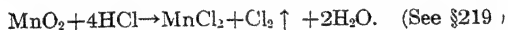
525. Occurrence and Preparation. Manganese, like chromium always occurs combined, the chief ore being pyrolusite,

MnO₂, which is rather abundant and widely distributed, but which does not occur in large quantities in the United States, the most important mines being in Russia, Spain, India and Brazil. Other oxides occur and they may be reduced by heating them to a high temperature with charcoal or aluminum in an electric furnace, some manganese carbide being formed when charcoal is used.

526. Properties and Uses. Manganese resembles cast iron, being hard, grayish, and brittle. It has a brilliant luster that disappears in moist air. Powdered manganese decomposes water at 100° and is superficially oxidized. It dissolves in dilute acids and with other metals forms several important alloys such as spiegel iron, ferromanganese, manganese bronze, etc., those of iron and manganese being used in the manufacture of Bessemer steel.

COMPOUNDS OF MANGANESE

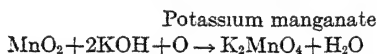
527. Manganese Dioxide is the most important compound of manganese. It is a black solid occurring in an impure condition as pyrolusite. By heating manganous nitrate, Mn(NO₃)₂, to 155°, manganese dioxide is obtained pure, and vapors of nitrogen tetroxide are given off. It is used in the manufacture of glass and in preparing oxygen, chlorine, manganese compounds and alloys. When heated with hydrochloric acid *manganous chloride* is formed and chlorine is given off.



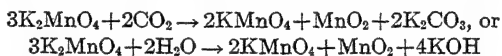
The chloride is pink and will unite with certain other chlorides to form double chlorides as (NH₄)₂MnCl₄. *Manganese oxide*, MnO, gray green in color; *manganic oxide*, Mn₂O₃, *manganous-manganic oxide*, Mn₃O₄, which is red; *manganic anhydride*, MnO₃, and *permanganic anhydride*, Mn₂O₇, are not as important as manganese dioxide and will not be described in detail.

528. Of the Permanganates, or salts of permanganic acid, *potassium permanganate* is the most important and best known.

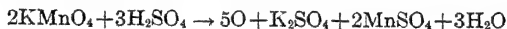
It is a reddish purple solid forming shining crystals that sometimes appear greenish black. It is made by oxidizing manganese dioxide in the presence of a base, the oxygen being supplied by the air, by potassium chlorate or potassium nitrate a typical reaction being expressed by the following equation:



When potassium manganate is treated with sulphuric acid, carbon dioxide or water, it is changed to the permanganate.



Potassium permanganate is used in many cases where a powerful oxidizer is needed as in the purification of water and sewage, as a disinfectant, in bleaching, dyeing and in purifying such gases as hydrogen, ammonia, carbon dioxide, etc. The color and odor may be removed from cistern water by the addition of potassium permanganate. When organic matter is present in water it may be detected by the addition of a little sulphuric acid and a drop or two of potassium permanganate after which the solution is warmed. The action between the permanganate and the acid may be written as follows:



The liberated oxygen attacks the organic matter and the solution becomes colorless or nearly so.

OTHER MANGANESE COMPOUNDS

529. Potassium Manganate, K_2MnO_4 , formed as in the first operation to make the permanganate, is treated with water and evaporated to crystallization when small greenish black crystals are formed. All manganates are salts of the hypothetical manganic acid.

Manganese carbonate, MnCO_3 , may be made from the residues when chlorine is made by the action of manganese dioxide and

hydrochloric acid. The salt is a whitish powder with a pale rose tint, which when heated in air gives off carbon dioxide and is converted into red oxide of manganese.

Manganese sulphate, MnSO_4 , is a pink salt crystallizing with two molecules of water of crystallization, and is formed by dissolving manganese carbonate in sulphuric acid. As the temperature is raised the water passes slowly off.

Manganese sulphide, MnS , is a flesh colored precipitate formed when ammonium sulphide is added to a solution of a manganous salt, which serves to distinguish it from all other sulphides.

RADIUM

530. Radium, as the chloride or bromide, may be obtained in a pure state from pitch-blende or in a less pure state from such rare minerals as samarskite, fergusonite or cleveite, which contain varying amounts of uranium, thorium, cerium, yttrium, etc., the amount from uranium oxide being about 1 gram from 3 tons of the ore. The uranium becomes recharged in a few months and this may be repeated any number of times. The amount of radium contained in these minerals is very small, often less than one part in 100,000,000. It is one of the rarest elements, the only ones that occur in smaller amounts being, possibly, krypton, xenon and actinium, the last of which has not been produced in sufficient amounts to be weighed.

Nearly 5 ounces of radium have been produced in the U. S. In 1914 it was estimated that the carnotite ores of the U. S. would produce $3\frac{1}{2}$ ounces of radium, but present estimates place the total at 20 ounces. The production of $\frac{1}{2}$ ounce per year is the maximum production in the U. S. at present. The supply comes from Colorado and Utah.

It has been found that radium salts give off 3 kinds of rays known as the alpha rays α , beta rays β , and gamma rays γ . (See Fig. 142.) These differ both in their penetrating power and in the manner in which they are affected by a magnetic field.

The alpha particles are positively charged and have very little penetrating power. The beta rays are a stream of electrons and are more penetrating than the alpha rays. The gamma rays are not affected by the magnetic field and are practically the same as X-rays.

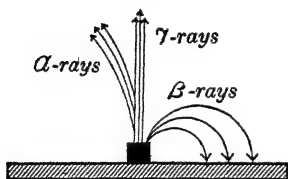


FIG 142 Radium Gives Off α , β and γ Rays

The rays act upon the air making it a conductor of electricity; they fog a photographic plate even though opaque substances intervene; they produce sores upon the body and if the exposure to the rays

is long enough the scars are permanent, although the sores may not appear until several weeks after the exposure. Particles of radium are thrown from the main mass with enormous velocity. These particles may be seen by using a spinthariscopes which consists of a zinc sulphide screen and a double convex lens giving a magnification of 10 to 20 diameters. (See Fig. 143.) A small speck of radium is placed between the screen and the lens and from this speck small particles are thrown off against the screen. To the naked eye the effect is a soft glow but the lens makes the small flashes of light appear like those produced by flint and steel. The spinthariscopes may also be used with a compound microscope using a 16 mm. objective and a $5\times$ or $7\frac{1}{2}\times$ eyepiece, giving 50 or 75 diameters. The heating effect produced by this bombardment is enormous when compared with the mass of radium, and it has been estimated that one gram of radium would give off as much heat as 300,000 grams of coal. Radium salts are usually from 3° to 5° warmer than the surrounding atmosphere.

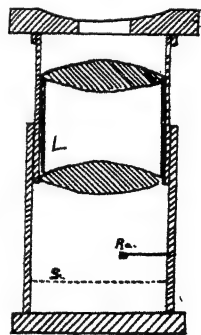


FIG. 143.
A Spinthariscopes

This radio-activity is independent of all chemical or physical conditions, heat or cold and chemical changes having no effect upon the activity of the particles. Rutherford has advanced the theory that the atoms of radio-active substances are slowly disintegrating into simpler substances. The radio-active elements, uranium, thorium and radium, have the greatest atomic weights of any known elements whose atomic weights have been determined. See table. When the atom disintegrates a new substance is formed, and the new substance further disintegrates until a stable combination is reached. It has been estimated that radium loses half its activity in 1280 to 2000 years so that it must be continuously formed or radium will eventually cease to exist.

531. When Radium Disintegrates the alpha particles have been proven to be positively charged helium atoms. Another gas known as Niton is produced at the same time. This gas has a molecular weight of 222. Niton is frequently called radium emanation. This decomposes into a substance called radium A producing a second helium atom and disintegration continues, forming radium B, C, D, and E, each of which forms another helium atom. Radium F then disintegrates into radium G having an atomic weight of 206 known as radio lead. This is no longer radio-active and undergoes no other changes. It has all the properties of ordinary lead except a lower atomic weight and for this reason was at one time included in the list of elements as the second variety of lead

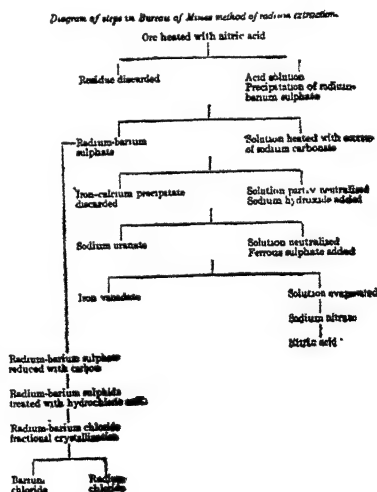


FIG. 144. Extraction of Radium.

although this practice has been discontinued. Radium itself is derived from the disintegration of uranium and when the radium salts have been extracted from the uranium ores the exhausted ores will again become radioactive and more radium may be extracted.

532. Radium is Used in three ways (1) in medicine, particularly in the treatment of cancer, where its value is not satisfactorily proven; (2) as luminous paint, (3) the low grade radium residues are used as fertilizers.

Radium paint consists of 0.4 mg of RaBr_2 mixed with 1 to 2 g. of phosphorescent ZnS . This is sufficient to last for 2 years, when the ZnS is worn out. The radium may be recovered and used again. (Fig. 145.)



FIG. 145. A Radiolite Watch

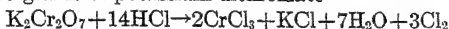
533. Electron Theory. The question naturally arises, What is the source of uranium? One theory concerning the constitution of matter is known as the electron theory, which, according to J. J. Thompson, is essentially as follows: The atom is built up of electrons or small particles highly charged with electricity. The positive electrons are thought to form the nucleus of the

atom, around which the negative electrons are rapidly rotating. The difference in the various atoms would consist simply in a difference in the number of electrons present, rather than in a difference in composition. According to the theory, the hydrogen atom is supposed to contain 2000 electrons and the other atoms contain a proportionate number according to their atomic weight. Thus oxygen would contain 32,000 electrons and uranium (238.2) would contain 476,400. The number of positive electrons in the atom is thought to be equal to the number of negative electrons, since the atom is believed to be electrically neutral.

It is not difficult to see that if the electrons are present in large numbers some might be split off, thereby changing the substance. Thompson succeeded in reversing the process and has added electrons to elements of low atomic weight, thereby producing elements of higher atomic weight. What the future work along this line of research may lead to no one can tell absolutely, but it may sometime be possible to produce any element desired by the addition or subtraction of electrons from other elements.

534. Problems.

1 Write the quantitative equation for the reaction of hydrochloric acid with 40 grams of potassium dichromate



2. Write the quantitative equation for the reaction of sulphuric acid and alcohol with 50 grams of potassium dichromate (§522).

3. How much hydrochloric acid is required to react with 75 grams of manganese dioxide? (§527)

4. Write the quantitative equation for the formation of 100 grams of potassium manganate from potassium hydroxide, manganese dioxide and oxygen. (§528)

5. How much potassium permanganate is formed by the action of 66 grams of carbon dioxide upon potassium manganate? (§528)

6. How much potassium permanganate is formed when 500 grams of potassium manganate react with water? (§528).

7. How much sulphuric acid is required to react with 80 grams of potassium permanganate? (§528).

CHAPTER XXIV

THE PERIODIC LAW

535. Early Attempts to Classify the Elements. The student has observed that certain elements have been selected for treatment in the same chapter and that comparisons have been made in several cases. This has been most prominent in the chapter on the halogens and in that on phosphorus, arsenic, antimony and bismuth. The fact that some of the elements are related in their general properties, was noticed many years before it was thought to have any important bearing on theoretical chemistry. As early as 1829 Dobereiner noticed that certain elements may be arranged as triads or groups of three elements, in which the atomic weight of the second element is the arithmetical mean between the first and third. The properties of the second element are intermediate between the other two. This may be seen in several instances of which the following are good examples:

Chlorine 35 46, bromine 79 92, iodine 126 92

$$\frac{35 \quad 46 + 126 \quad 92}{2} = 81 \quad 19$$

Sulphur 32 06, selenium 79 2, tellurium 127 5

$$\frac{32 \quad 06 + 127 \quad 5}{2} = 79 \quad 78$$

Lithium 6 94, sodium 23 00, potassium 39 10

$$\frac{6 \quad 94 + 39 \quad 10}{2} = 23 \quad 02$$

Calcium 40 07, strontium 87 63, barium 137 37

$$\frac{40 \quad 07 + 137 \quad 37}{2} = 88 \quad 72$$

Phosphorus 31.04, arsenic 74.96, antimony 120.2

$$\frac{31.04 + 120.2}{2} = 75 \quad 62$$

536. The "Law of Octaves." In 1864 Newlands observed that if the elements were arranged in the order of their atomic weights similar elements were separated by about equal distances, and he formulated his "Law of Octaves," comparing the elements to the notes in music, since every eighth element seemed to belong to a natural group whose members resembled each other more than they did the other elements. The law was not accurate in every case and has been abandoned.

537. The "Periodic Law" was first propounded by Mendelejeff, a Russian chemist in 1869, and revised by Lothar Meyer in 1870. The substance of the law is somewhat as follows. The properties of all elements are periodic functions of their atomic weights. It means that the atomic weight of an element determines what properties that element may have, and that if the atomic weights of two elements differ their properties must differ.

538. Arrangement of the Elements. The elements are divided into 12 series arranged in horizontal lines according to the atomic weight and divided into 9 groups arranged in vertical columns, the members of which have in most cases rather similar properties. 'It will be noticed that the first series is very incomplete, but we may take series 2, 3, and 4 for comparison. In the first group will be noticed lithium, sodium and potassium. A careful study of their properties will show that they are very similar in their chemical behavior. In group V the similarity in the compounds of nitrogen and phosphorus has been noticed, and by going into some of the other series we find that these are in many respects similar to arsenic, antimony and bismuth. In Group VI will be found oxygen and sulphur. Many oxygen compounds have a corresponding sulphur compound as may be noticed by recalling water, H_2O , and hydrogen sulphide, H_2S ; carbon dioxide, CO_2 , and carbon disulphide, CS_2 , etc. In group VII are found fluorine, chlorine, bromine and iodine whose great similarity may be seen by referring to the comparative table

TABLE SHOWING THE PERIODIC ARRANGEMENT OF THE ELEMENTS

	Group 0	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII
Series	No Compounds formed	ROH RCl R ₂ O	R(OH) ₂ RCl ₂ RO	R(OH) ₃ RCl ₃ R ₂ O ₃	RH ₄ RCl ₄ RO ₂	RH ₃ RCl ₃ R ₂ O ₃	RH ₂ RCl ₂ RO ₂	RH RCl R ₂ O ₇	R ₄
1		H, 1 008							
2	He, 4	Li, 6 94	Cl, 9 1	B, 10 9	C, 12 005	N, 14 01	O, 16	F, 19	
3	Ne, 20 2	Na, 23 00	Mg, 24 32	Al, 27 1	Si, 28 3	P, 31 04	S, 32 06	Cl, 35 46	
4	A, 39.9	K, 39 10	Ca, 40 07	Sc, 45 1	Ti, 48 1	V, 51 0	Cr, 52 0	Mn, 54 93	$\left\{ \begin{array}{l} Fe, 55 84 \\ Co, 58 97 \\ Ni, 58 68 \end{array} \right\}$
5		Cu, 63 57	Zn, 65 37	Ga, 70 1	Ge, 72 5	As, 74 96	Se, 79 2	Br, 79 92	
6	Kr, 82 92	Rh, 85 45	Sr, 87 63	Yt, 89 33	Zr, 90 6	Cb, 93 1	Mo, 96		$\left\{ \begin{array}{l} Ru, 101 7 \\ Rh, 102 9 \\ Pd, 106 7 \end{array} \right\}$
7		Ag, 107 88	Cd, 112 4	In, 114 8	Sn, 118 7	Sb, 120 2	Te, 127 5	I, 126 92	
8	Xe, 130 2	Cs, 132 81	Ba, 137 37	La, 139	Ce, 140 25	Pr, 140 9	Nd, 144 3		$\left\{ \begin{array}{l} Sb, 150 4 \\ Eu, 152 \\ Gd, 157 3 \end{array} \right\}$
9				Er, 167 7		Yb, 173 5			
10					Lu, 175	Ta, 181 5	W, 184 0		$\left\{ \begin{array}{l} Os, 190 9 \\ Ir, 193 1 \\ Pt, 195 2 \end{array} \right\}$
11		Au, 197 2	Hg, 200 6	Tl, 204 0	Pb, 207 2	Bi, 208			
12	Nt, 222		Ra, 226		Th, 232 15		U, 238 2		

given in Chapter 11. In group VIII at the end of series 4, 6, 8 and 10 are found 3 elements which seem to form small independent groups, but these small sub-groups are not found after the other evenly numbered series, although they might naturally be expected. Series 2, which, before the discovery of helium, consisted of only 7 elements, is known as a short period, while the third and fourth series with the sub-group in series 4, group VIII, is known as a long period. The recently discovered gases of the atmosphere seem to fall most naturally into series 2, 3, 4, 6 and 8 in group 0 since their valence is 0.

539. Vacant Spaces. In a uniform table several more elements should be discovered to fill in the gaps that may be noticed. Series 2 and probably series 12 should each have a sub-group of 3 elements in group VIII, while possibly all of the odd numbered series should have 2 or 3 elements in the sub-groups of group VIII, and many other gaps in the table should be filled for completeness. That the prediction of elements is possible may be seen from the fact that the discovery of scandium, gallium, germanium, samarium, etc., and their probable properties were foretold before the elements themselves were known.

540. Combining Power as Shown by the Table. A careful study of the elements of the table will show that their atomic volume, that is their atomic weight divided by their density, and their volatility decrease as we pass from either end of the series toward the middle. The power to combine with oxygen increases from left to right as may be seen from certain oxides selected from many— H_2O , MgO , B_2O_3 , CO_2 , P_2O_5 , SO_3 , I_2O_7 , Os_2O_8 ; while the power to combine with hydrogen seems to be limited to groups IV, V, VI, VII and increases as we pass from right to left, as seen in HF , H_2O , NH_3 , CH_4 ; but hydroxides of the first three groups are well known, and the power to combine with hydroxyl increases from left to right, NaOH , Ca(OH)_2 , Al(OH)_3 , etc. Groups I, II and III are more metallic and hence form the strongest bases; groups VII, VI, V are non-

metallic and are acid-forming, while group IV is not strongly marked as either metallic or non-metallic and its members form both acids and bases. Groups VIII and 0 do not enter the general scheme but serve to connect the strong acid forming elements with the strong base forming elements. With the exception of radium the newly discovered elements seem to fall into a group by themselves. They do not form compounds in the ordinary sense of the term and if they have any place at all in the table, it would seem natural to place these non-valent elements in spaces to serve as connecting links between the negative univalent halogen elements and the positive univalent alkali metals. An apparent exception will be seen in argon, having an atomic weight of 39.9 thus placed before potassium which has an atomic weight of 39.10, but the latest results show that the atomic weight of tellurium is 127.5 and not 125.2 as formerly assigned, yet it must stay in group VI, while iodine, 126.92, falls in group VII, where it must remain.

541. Hydrogen and Radium. The place of hydrogen has been questioned. Since it is univalent it must fall into either group I or VII. In physical properties it resembles the halogens more closely than it does the alkali metals. In chemical properties it is different from either group, although in acids it is easily replaced by the alkali metals, and in organic compounds by the halogens.

The new element, radium, to which the atomic weight of 226 has been assigned seems to belong to group II and falls naturally into series 12 along with thorium and uranium, two other radio-active elements; and niton is placed in group 0 with the other non-valent elements.

542. Atomic Numbers. The latest arrangement of the elements is based upon the atomic numbers. This system was first described by Moseley in 1913, and is based upon the behavior of X-rays when they are allowed to fall upon different metals. The reflected rays form a spectrum and give characteristic lines. The spectra are photographed and the rate of vibra-

tion of the rays is determined. A factor or Q value is determined, and this value differs by unity for the different elements. Placing hydrogen at the lowest value, 1, some of the other elements are helium, 2; lithium, 3; glucinum, 4; boron, 5; carbon, 6; nitrogen, 7; oxygen, 8; fluorine, 9; neon, 10; etc. The atomic numbers are determined by adding 1 to the Q values, and when determined denote the position of the element in the series as determined by the X-ray spectrum.

Since liquid and gaseous elements do not act in the same manner as metals the atomic numbers of these elements are determined by indirect methods. For example, the value for chlorine or bromine might be learned from the sodium compounds, sodium chloride and sodium bromide. Since the value for sodium may be determined directly, the value for the chlorine may be determined by subtracting the sodium lines from those of sodium chloride, the difference being the lines for chlorine.

543. Comparison of Periodic Table and Table of Atomic Numbers. From the periodic table it will be noticed that in three places the elements are not exactly in order of atomic weight; argon comes before potassium; cobalt comes before nickel; and tellurium comes before iodine. In the table of atomic numbers argon is 18; potassium, 19; iron, 26; cobalt, 27; nickel, 28; tellurium, 52 and iodine, 53. There is only one gap between molybdenum, 42, and ruthenium, 44; and among the rare earths, indicated in the periodic table as having weights from about 140 to 180, with the exact number a little in doubt, there are according to Moseley only 15 possibilities. If all the gaps in the periodic table could be filled in groups O to VII with 3 in the even series of group VIII there would be 114 elements, while if the odd series of group VIII should also have three elements each the total would reach 132. Moseley stated before his death that there could be only 92 elements according to the atomic numbers, but this is now taken to apply to types of elements, rather than to the exact number.

CHAPTER XXV
APPLIED CHEMISTRY
CARBOHYDRATES, FATS AND PROTEINS

544. Food Defined. A food may be defined as a substance taken into the body for the purpose of adding to or maintaining the heat and energy of the body. If a substance contributes to neither heat nor energy it cannot be classed as a food.

545. Pure Food. A food, to be considered pure, must not contain any substance that acts upon the body injuriously to produce distress, sickness or death. It must not contain any deleterious or poisonous substance, and must not be adulterated in any way either to deceive the purchaser or to cause a reduction in the food value. Nor can a pure food contain any preservative used in such a manner as to enable the dealer to sell as food any substance that is partly or wholly decomposed; although the well known preservatives, such as sugar, salt, spices, etc., are not considered as being added to deceive.

546. Chemical Elements in Food. The elemental substances occurring in foods are chiefly carbon, hydrogen, oxygen and nitrogen, found in all animal and vegetable foods. Certain foods contain small amounts of calcium, phosphorus and silicon used in feeding the bones and teeth; and iron, sodium and chlorine, found in the blood. Other elements occur in minute quantities. These elements are not used in a free condition, but are found in compounds, of which we have several well-known groups used as foods.

547. Classification of Foods. Foods are divided into four classes—carbohydrates, fats, proteins and mineral matter. Some of the compounds are simple in structure, while others are very complex and are not well understood.

548. Carbohydrates Defined. Carbohydrates are compounds of carbon, hydrogen and oxygen, the last two being

found in the same proportion as they are found in water, but they are not thought to have the hydrogen and oxygen combined as water in the compound. There are some exceptions to the rule since formaldehyde, CH_2O , is not classed as a carbohydrate and rhamnose, $\text{C}_6\text{H}_{12}\text{O}_5$, is. Carbohydrates are mostly of *vegetable origin*. As a food carbohydrates supply energy to the body.

549. Carbohydrates Classified. There are three main divisions of carbohydrates, (1) Monosaccharides, or simple sugars, where the name of the monosaccharide depends upon the number of carbon atoms in the molecule. The most important of these are the hexoses, $\text{C}_6\text{H}_{12}\text{O}_6$, including glucose (called also dextrose and starch sugar), levulose and fructose; and to a small extent one of the pentoses called arabinose, $\text{C}_5\text{H}_{10}\text{O}_5$, (2) Polysaccharides, or complex sugars, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, including cane sugar, sugar of milk, maltose, etc. (3) Polysaccharides, not resembling sugar, including (a) cellulose and starch, $(\text{C}_6\text{H}_{10}\text{O}_5)_x$, (b) dextrin, $\text{C}_6\text{H}_{10}\text{O}_5$, and certain gums, as gum arabic, which has the same percentage composition as cane sugar and the same formula, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$. The percentage composition of carbohydrates is given in §557.

550. The Carbohydrates Used as Foods include sugars, starches and cellulose. There are about 200 sugars known to chemistry but the most prized is *sucrose* $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, found in sugar cane, sugar beets, maple sugar, etc. Dextrose, levulose, milk sugar and meat sugar are all consumed in foods, but they are less sweet than sucrose.

Starch, $(\text{C}_6\text{H}_{10}\text{O}_5)_x$, occurs in various plants, such as potatoes, grains, etc. The different starches are insoluble, but they are changed chemically in the sap of plants, in the sprouting of grain, and may to some extent be acted upon by the pancreatic juice during digestion, changing to some form of sugar, chiefly dextrose and maltose, which are more easily digested than cane sugar, since the latter has first to be changed into dextrose and levulose before being digested. The formula for starch is

written $(C_6H_{10}O_5)_x$, and not $C_6H_{10}O_5$, because the methods of determining exact molecular weights fail to work with starch and we can learn from analysis only the proportions in which the elements occur.

Cellulose, $C_6H_{10}O_5$, occurs in wood and vegetable fibers, and although consumed in rather large quantities along with food, is insoluble and is not assimilated, except when very tender. It probably serves a useful purpose by adding to the bulk of the material passing through the intestines, thereby helping to prevent constipation.

The chemical steps by which starch, cellulose, etc., are made in the plant are not fully understood. We know that plants take in air through microscopic openings in the leaves, called "stomata." Water ascends from the roots, through the stems and veins of the leaves, and finally is brought into contact with carbon dioxide in the cells of the leaves. In these cells is a green substance known as chlorophyll which is believed to act as a contact agent, while the sunlight supplies the energy necessary for the chemical union. Probably there are several steps in the process, but the final result may be expressed for starch by the equation



The surplus oxygen, not being needed by the plant, passes out into the atmosphere through the stomata. This chemical action is known as "photosynthesis," which means "light synthesis"—a synthesis aided by sunlight.

Fig. 146 shows what is called the carbon dioxide and oxygen cycle in nature. Animals take in oxygen from the air, and exhale carbon dioxide, which is taken up by the plants as just explained, and the surplus oxygen is given out again to the atmosphere.

551. Extraction of Starch From Corn. The separation of starch is largely mechanical. The corn germ, consisting of protein, oil and gluten (not the same as wheat gluten, see §629),

is surrounded by starch which will be converted into sugar if the germ sprouts. (See Fig. 147.) The corn is steeped in dilute sulphurous acid, softened, broken into coarse particles, and the

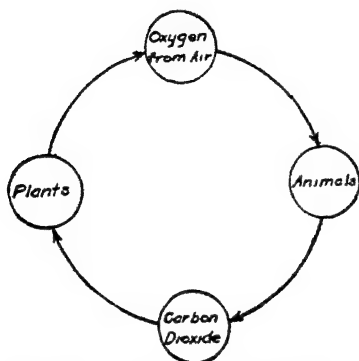


FIG. 146 Carbon Dioxide and Oxygen Cycle.

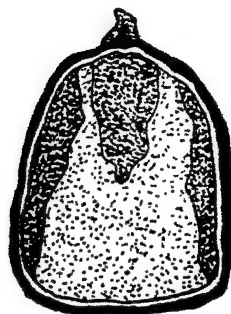


FIG. 147. Corn Structure.

germs are separated from the starch and hulls by being conducted into deep tanks of water where the germs float and the starch and hulls sink. Corn oil is extracted from the germs by pressure, and is used for soap, or if refined may be used for cooking. The germs which contain some oil, much protein and starch and some mineral matter are made into oil cake, used for cattle food.

The removal of the starch is accomplished by agitation with water, and the coarser particles are reground. It is then passed with water through long wooden troughs, slightly inclined. The starch settles, and from time to time is removed and dried.

Fig. 148 shows a comparison of the grains of starch obtained from corn, potatoes, wheat and rice. Potato starch is distinguished by the large grains, $\frac{1}{300}$ of an inch in diameter, while wheat starch averages $\frac{1}{1000}$ of an inch, and rice starch has much

finer grains. Starch is insoluble in water, but when boiled it swells and bursts. (See Fig. 149.) This gives a sort of transparent jelly which, when further diluted, passes through filter paper like a solution, but, since the starch has not reached molecular proportions, is not a true solution, but is called *colloidal suspension*

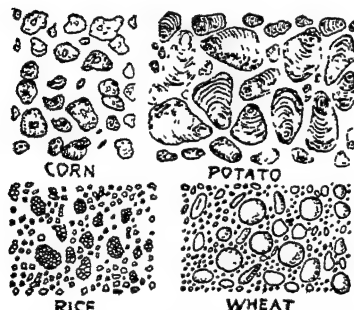


FIG. 148. Comparison of Starch Granules.

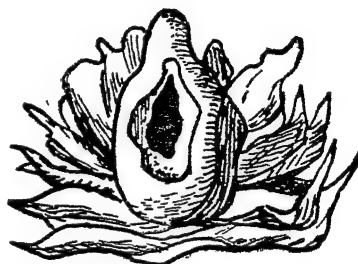


FIG. 149. A Granule of Starch Bursts Open by Boiling

552. Making Sugar From Starch. The starch is suspended in water, a small amount of hydrochloric acid is added, and the mixture is heated by steam under pressure. The starch takes up a small amount of water, forming at first dextrin and dextrose. On further heating the dextrin changes into maltose and dextrose, and finally the maltose changes into dextrose, so that the final equation might be written



With prolonged heating almost all of the starch is changed into dextrose. What crystallizes out is known as corn sugar. The acid in the syrup is then neutralized with soda ash. The liquid is then filtered first through canvas bags, then through animal charcoal, into large tanks, the odor being removed. The syrup is then concentrated in vacuum pans and is known as corn

syrup, often called glucose, but is a mixture of dextrose, (glucose) dextrin, and similar sugars in smaller amounts.

553. Treatment and Use of Corn Syrup. Corn syrup has very little flavor and is, therefore, mixed with molasses from the sugar refiners, which is too strong to use alone, the mixture giving table syrup. Glucose is highly nutritious, is readily digested and assimilated and has a calorific value of 1777 per pound. The greatest objection to glucose is that it is usually sold under another name, or is used as an adulterant for cane sugar in candy making, etc. There are no valid objections to it if sold for what it is. Fully 1,000,000,000 pounds are made annually.

554. Sucrose is obtained from the sugar cane, sugar beet, sugar maple, sorghum, the Java Palm, etc. The sugar cane is cut, pressed, and the sugar is dissolved out with water, while lime is added to make the syrup alkaline. With beets the process is about the same except that the sugar is removed more by diffusion. Phosphoric acid is added to the syrup containing the lime, forming calcium phosphate which carries down the impurities. It is then filtered through animal charcoal, evaporated in vacuum pans (see fig. 150) and crystallized. A little Prussian blue is added to remove any traces of yellow color. The uncrystallizable portion is known as molasses.

555. Other Sugars. *Maple Sugar.* Maple sugar is made by tapping the sugar maples, boiling the sap to a thick syrup, and stirring the syrup until it crystallizes as maple sugar. The flavor is different owing to small amounts of substances not found in the cane or beet sugar. Maple sugar is highly prized on account of its delicate flavor, so that

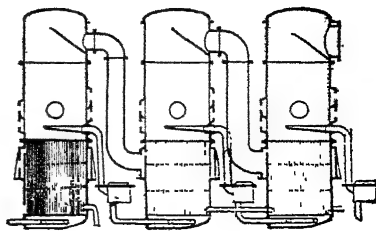


FIG. 150. Vacuum Evaporators.

it very frequently is adulterated, a fair imitation being made from brown sugar and mapelene.

Honey is a natural syrup containing dextrose, levulose and sucrose, but no maltose, and is obtained from plants by bees.

556. Sugar as Food. Some use sugar only for flavoring, or eat candy merely to gratify the taste. Sugar alone has a calorific value of 1777 per pound, while chocolate, with which it is most frequently combined, has a calorific value of 2684. Nuts, which are frequently added to the candy have a calorific value nearly as high as chocolate, as compared with 1,000 for meats and 500 for vegetables and fish. In fact one pound of chocolate creams and two-thirds of a pound of peanuts will give almost enough nourishment for a day, and in almost the right proportion—85 grams of protein, 149 grams of fat and 403 of carbohydrates, as against the necessary 100 of protein, 100 of fats, and 420 of carbohydrates. However, a large part of the carbohydrates should be present as starch, instead as the almost perfectly soluble sugar. Although sugar is stimulating for a short time it is quickly used up in the system and is not satisfying. Peanuts, also, are not so desirable in large quantities, since they contain other constituents that frequently cause distress. It is better to eat both candy and nuts as a part of a meal rather than as a supplementary lunch between meals.

557. Percentage Composition of Carbohydrates, Fats and Oils Used in Foods.

<i>Name of Substance</i>	<i>Carbon</i>	<i>Hydrogen</i>	<i>Oxygen</i>
Cane sugar and Maltose, $C_{12}H_{22}O_{11}$	42 105	6 432	51.462
Glucose, Dextrose, Levulose, $C_6H_{12}O_6$	40 000	6 666	53 333
Starch, Dextrin, Cellulose, $C_6H_{10}O_5$	44 444	6 172	49.384
Fats and Oils (average)	76 5	11 9	11 5

558. Fats and Oils. From the preceding table it will be seen that the fats and oils have a much smaller percentage of oxygen with a corresponding increase in the percentage of carbon and hydrogen. They have a complex structure and are composed of glycerin, $C_3H_5(OH)_3$, and fatty acids. The oils are often changed by the action of light and air so that the free acids are liberated, and if these develop a distinct odor and taste they are called rancid. Not all acid oils are rancid, but all rancid oils are acid. During digestion the glycerin separates from the acids, but after absorption these are recombined to form the body fats. Animal and vegetable fats are very similar in composition.

Hydrogenation of Oils. Oils that have become rancid, or fats that are too rancid or too soft to use in food products may be sweetened and solidified by passing pure hydrogen through the warm oil or fat containing a catalytic agent, such as one of the nickel salts. Nickel oxide, nickel sulphate, nickel formate, etc., are used as catalytic agents. The addition of the hydrogen acts chemically as a reducing agent, lowering the percentage of oxygen. After the hydrogen has been taken up by the oil, it is filtered to remove the nickel salts.

If oil is kept for a long time at a low temperature it separates into a solid and a liquid layer. These may be separated by filtration, and if warmed may be recombined, but the properties are not exactly the same after the recombination. Solid fat may be heated to a point where only a part of it is converted into oil. If this is separated by filtering the solid part is called *stearin*. When the decomposition is carried further, glycerin and one or usually more of the fatty acids may be obtained. Fats that are liquid at ordinary temperatures are known as oils, such as oleic acid, found largely in lard. Other acids, such as stearic and palmitic form solid fats, such as beef and mutton tallow. These acids do not occur free in fats and oils but are combined with about 8% of glycerin, forming stearin, palmitin, olein, etc.

Pure glycerol (glycerin) is a viscous, colorless, sweet syrup that solidifies at low temperatures and boils at 290° with decomposition. Its specific gravity is 1.265 at 15° . Very often substitutes for glycerin are used in toilet preparations and elsewhere, such as nulomoline, made from cane sugar, white Karo syrup, etc.

559. Decomposition of Fats. Fats are commonly decomposed by heating with steam, by alkalies, by the action of bacteria or the digestive fluids. If heated strongly acrolein is set free from the decomposition of the glycerin. This is very irritating to the eyes, causing tears.

In soap making, (see §766, ff.) the fat is decomposed by alkalies and the glycerin may either remain in the soap, or it may be separated, purified, and sold as a separate product.

560. Other Ingredients of Oils. Most oils contain a small amount of flavoring matter. Some, as croton oil, contain poisonous ingredients, while others, such as cod and castor, are used as medicines.

561. Oils Used as Foods. The chief oils used as foods are derived from almonds, cocoanuts, cottonseed, corn, hazelnuts, olives, peanuts, rapeseed, sesame, sunflower seed and poppy seed, the one used in any locality depending upon the individual taste, and the cost and ease of obtaining the oil. In the United States the oils most commonly used are olive, corn, cottonseed and coconut.

562. Olive Oil. The oil obtained from hand-picked, unbruised olives, cold-pressed, is a neutral oil, and is known as "virgin oil." The residue is heated and again pressed, giving an inferior oil that has to be purified before it can be used as a food. The residue from the hot presses may be treated with carbon disulphide or petroleum ether, and yields a third quality of oil, that is not suitable for food but is good for soap.

563. Adulteration of Olive Oil. Since olive oil is expensive when pure, various oils are used as adulterants. In the United States cottonseed oil is used for this purpose, while in Europe

sesame or peanut oil and occasionally castor oil, lard oil, fish oil or even petroleum are used. If the foreign oil is not over 20 to 30% it cannot be detected by the taste.

564. Properties of Olive Oil. Olive oil has a pale yellow or greenish yellow color. Its specific gravity varies from 0.915 to 0.918 at 15° C. Its chemical formula may be expressed as $C_{26}H_{48}OH$. It is soluble in ether, chloroform and carbon disulphide, and sparingly soluble in alcohol. Olive oil becomes rancid upon exposure. Olive oil is chiefly olein with from 3 to 20% palmitin, and small amounts of arachin (from peanut oil) stearin, linolein and cholesterin. According to Food Inspection Decision No. 139, olive oil is the only oil to which the name "sweet oil" may be applied legally. It may not be applied to a mixture of olive and cotton seed oils.

565. Coconut Oil. This oil is made from cocoanut meats by pressure. It more nearly resembles butter fat and is used for making artificial butter, and when deodorized as a filling for chocolate creams. It is a white, semi-solid, lard-like fat, turning to a liquid at 20 to 25° C. It is soluble in alcohol and ether.

566. Corn Oil is made from the germs of the corn and although it was formerly a product of the distilleries, it is now made largely in the starch and glucose works. The whole grain contains about 4.1% oil. The germs alone contain about 53.1%, yielding about 40%.

Corn oil is clear, of a pale yellow color, and when properly made does not require refining for commercial purposes. If badly prepared and allowed to stand in contact with albuminous matter it undergoes fermentation, forming free fatty acids and becoming dark in color making it unsuitable even for soap making in that condition.

The specific gravity of corn oil varies from 0.925 to 0.927. The saturated fatty acids present are palmitic, stearic and arachidic with some linolic and oleic.

Well refined corn oil tastes like corn meal. It is used in making salad oils but owing to its taste is usually mixed with

other edible oils such as edible cotton seed oil. It is also used in the manufacture of oleomargarine.

567. Cottonseed Oil. Cottonseed oil is made from the meats of the cotton seed. The meats contain from 30 to 35% of oil. The meats are passed between heavy rollers, and are then cooked in steam jacketed kettles, and extracted in a hydraulic press with a pressure of 3,000 to 4,000 pounds per square inch. About 85% of the oil is extracted and the remainder is left in the oil cake, which is valuable for cattle food, since it contains about 38% protein. The oil is then refined by heating and agitation in large tanks with sodium hydroxide which combines with the free fatty acids and removes the resinous coloring matters. After the impurities settle, the clear yellow oil is drawn off, dried and filtered through Fuller's earth and deodorized. This is known as summer yellow. Winter yellow is made by chilling the summer yellow, crystallizing and separating the stearin and palmitin, which is sold as cottonseed stearin.

568. Properties of Cottonseed Oil. Cottonseed oil is odorless, resembling olive oil somewhat in color but more yellow. It has a specific gravity of 0.920 to 0.930 at 15°C. It is soluble in ether, chloroform, and carbon disulphide, and slightly soluble in alcohol.

569. Uses of Cottonseed Oil. Cottonseed oil is used largely in making lard substitutes, by melting 15 to 20% oleostearin in heated oil and cooling it suddenly by passing it over chilled rolls. Salad oil is made by chilling highly refined cottonseed oil until the palmitin crystallizes out and the oil is pressed out of this semi-solid mass. A ton of cotton seed contains about 50 pounds of oil, of which 45 pounds may be extracted.

570. Butter. Butter is made by churning cream that has been made acid by the action of bacteria. Butter averages about 84% fat, 12.8% water, 2% salt, the remainder being sugar, protein and coloring matter. Butter fat is about 5.25% glycerin, combined with several of the fatty acids, of which palmitic is about 38.61%, oleic about 32.5%, and the volatile

fatty acids about 20%. These probably give the characteristic flavor of butter, and occur in varying proportions, butyric acid 5.45%; myristic, 9.89% having the largest proportions, while lauric, caproic, stearic, dioxystearic, caprylic and capric vary between 2.57 and 0.32%. The fine flavor of butter is produced by introducing into the sweet cream a pure culture of the right bacteria. If other bacteria are introduced a disagreeable odor may be produced and the butter becomes rancid and cannot be used as food.

571. Renovated Butter. Poor butter is melted in large tanks, and by blowing air through it most of the odor is removed. The casein and the brine settle and the clear, sweet fat is drawn off and mixed with sweet milk and churned. It is not quite the same as true butter and is inferior in flavor.

572. Oleomargarine. Oleomargarine is a substitute for butter, in which the butter fat is replaced by cheaper fats. Oleo oil from lard heated to 45°C. and pressed, is mixed with cottonseed oil and milk and churned. Butter is often added to improve flavor and odor. Oleomargarine may or may not be colored, but it is a fraud to color it and sell it for butter. There is no objection to selling the uncolored product. There is a tax of 10 cents a pound if colored. It produces more heat than the genuine butter and is said to be somewhat more indigestible.

573. Nut Margarines. Later processes combine cocoanut oil and fresh milk, with or without the addition of other fats, producing various grades of nut margarines, differing somewhat in taste and composition from oleomargarine, described in the last section.

574. Proteins. The proteins embrace a large variety of food materials and are known by different names as they occur in different compounds. The general term covers the substances known as albumen, gelatin, gluten, etc., and includes substances that supply the available nitrogen to the body. Such substances as the white of eggs, lean meat, the gluten of wheat and rye, are known as proteins and will average about 16% nitrogen

with some sulphur and phosphorus. Egg albumen coagulates when boiled. The protein of the blood is in solution as long as the blood is in the body, but solidifies on exposure, and when washed is colorless and known as *fibrin*, while the liquid portion of the blood is called *serum*. *Proteins are necessary to build up and maintain the strength of the body and cannot be replaced by the other food materials.* Carbohydrates and fats are intended to furnish energy and heat for work and warmth and can to a large extent be substituted for each other but not for proteins.

575. Mineral Matter. The mineral matter of foods is found in the incombustible ash when food is burned. As found in the ash it is mostly insoluble, but as found in foods it occurs in such combination that it is soluble in the blood and is deposited where needed.

576. Calorific Value of Food. The calorific or fuel value of food is measured in *large calories*, i.e., 1,000 times the small calorie. It is, therefore, the *amount of heat required to raise the temperature of one kilogram of water one degree Centigrade.*

One gram of protein, fully oxidized, will produce 5.7 large calories, but as consumed in the body it produces only 4.1 calories, the same as a gram of carbohydrates, while a gram of fat will produce 9.3 calories.

The fuel value of a food is determined by using a bomb calorimeter. (See Fig. 151.) The food is completely burned in a capsule and the heat is transferred through

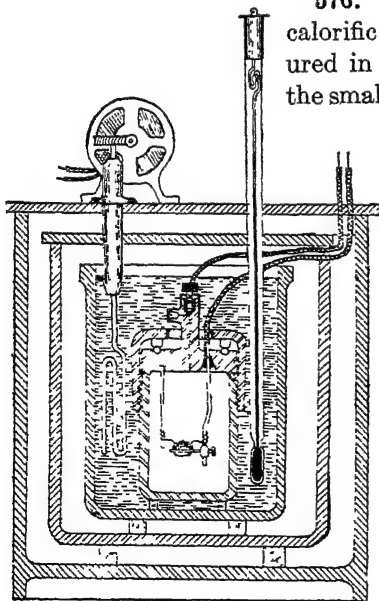


FIG. 151. Bomb Calorimeter.

the bomb to the surrounding water. The weight of the water in kilograms multiplied by the rise in temperature in degrees C. gives the number of large calories produced.

577. Candy Making. When cane sugar is heated in the presence of an acid it changes to dextrose and levulose, similar to glucose, as when tartaric acid or vinegar (dilute acetic acid) is added to candy. The same change occurs in the stomach. Candy made with glucose is not white, but slightly yellow, unless bleached with sulphurous acid, which is considered non-injurious in very small amounts, but if large amounts are used, or if the action is continued for a long time the kidneys are affected.

578. Chocolate is made from the cocoa bean, (Fig. 152)—from 25 to 40 beans growing in a single fruit which is about ten inches long and four inches wide. The beans are sorted, roasted, hulled and crushed. The germs are removed and the nibs or meats are ground, usually three times, to a thin paste which becomes hard on cooling and is about 50% fat, about half of which may be removed by moderate pressure and about 60% if the pressure is 4,500 pounds per square inch. This is known as cocoa butter and is used in chocolate bars and chocolate coatings. Sweet chocolate contains a larger proportion of sugar, starch and water, and a smaller proportion of fat, protein, theobromine, caffeine, fiber and ash than pure chocolate.

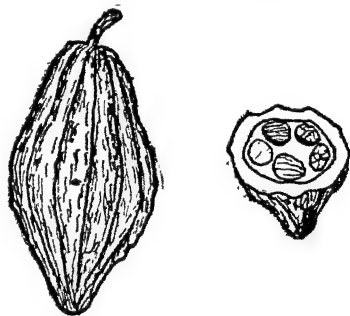


Fig. 152. Cocoa Fruit, with Cross Section Showing Beans.

579. Breakfast Cocoa is made by grinding chocolate from which part of the cocoa butter has been removed, otherwise it is too rich. The amount left in varies from 23 to 39%. Alkaline carbonates are usually added so as to make a better emulsion.

The Dutch process uses carbonates of potassium, sodium and magnesium, which remain in the cocoa when heated, while the German process uses ammonia or ammonium carbonate which is expelled when heated. The cocoa is then ground and is ready for use. The addition of the alkali holds the cocoa in suspension better and prevents precipitation. The composition of breakfast cocoas varies with the brand, but the general composition shows water, 2.70 to 6%; ash, 4.05 to 8.2%; fat, 23 to 39%; theobromin 0.66 to 1.36%; starch, fiber, etc., 4.66 to 30%; protein, 6.75 to 19.5%.

580. Adulteration of Cocoa. Cocoa is adulterated by removing a larger percentage of the fats and by adding ground hulls, which have no food or commercial value.

Adulteration of Chocolate. Chocolate is often adulterated by using beef stearin or cocoanut oil stearin to replace the cocoa butter, or by using a bean known as St. John's bread, which is sweet and agreeable in taste. Imitation chocolate may consist of gelatin and sugar colored with iron oxide and coated with shellac varnish, while sometimes aniline dyes are used.

581. Saccharin. Saccharin is not chemically related to the sugars. It is also known as garantose, and has at least a dozen different names. Chemically it is benzosulphimid, $C_6H_4(CO)SO_2NH$, and is made from toluene or thiosalicylic acid. It is a white, odorless, microcrystalline powder, from 500 to 550 times as sweet as sugar. Its sweet taste may be detected when one part is dissolved in 70,000 parts of water. It is soluble in 250 parts of water at ordinary temperatures, or in 24 parts at 100° C. It melts at 220° C. Saccharin has no nutritive value and can be taken in only very minute quantities. It may sometimes be used where sugar cannot, and is effective in killing the taste of nauseous substances.

It is illegal to use saccharin in place of sugar without labeling it as such since amounts might otherwise be consumed that would produce digestive disturbances. The use of saccharin in foods intended for the mitigation or cure of certain diseases,

where sugar cannot be used, is not prohibited, provided the foods are labeled to show their true purpose, and the presence of saccharin is declared upon the principal label. See Food Inspection Decisions No. 135 and 146.

582. Daily Ration. The average daily ration should consist approximately of 100 grams of protein, 100 grams of fat and 420 grams of carbohydrates, equivalent to about 1.37 pounds of total food value, and requiring about four pounds of ordinary food to furnish the necessary material. This amount is, however, somewhat deficient in heat, since it will furnish a little more than 3,000 calories while 3,500 are needed. Different individuals differ in the amounts needed and in their ability to digest different food materials. The *average final digestibility* is 91% for proteins, 95% for fats and 98% for carbohydrates, as they are found in the common foods. The actual work of digestion may, however, be hard and long when certain foods are eaten.

583. Milk as Food. Milk is one of the most important of all foods, averaging about 10% of the total amount consumed daily. Milk contains all four food constituents, and the total solids, which give the food value, vary from 9 to 17%, averaging about 13% while the remainder is water.

584. Fat in Milk. The fat of milk is in the form of very minute globules about $1/10,000$ inch in diameter, not dissolved, but in the form of an emulsion. The fat should not be less than 3% of the whole milk. It rarely exceeds 5% and in good milk averages about 4% of the whole milk or about 31% of the total solids. When milk is allowed to stand part of the fat rises as light cream, forming by volume $1/8$ to $1/5$ of all the milk. When a separator is used all of the cream may be removed.

585. Protein in Milk. When the cream has been removed the remainder is called skim milk. This contains all of the solids except the fat, and is relatively richer in proteins, carbohydrates and mineral matter than whole milk. If the skim milk stands the protein, called *casein*, separates as *curd*, and may be

made into cheese. The casein may be coagulated by either acid or rennet. The protein of milk varies from about 2 to more than 6%, averaging 3.3% of the whole milk, and constitutes about $\frac{1}{4}$ of the total solids.

586. Carbohydrates. The sweetish liquid remaining after the curd has been removed is known as *whey* and contains the sugar and mineral matter. By boiling the whey the sugar may be made to crystallize on sticks and is known as lactose or *milk sugar*. This varies from 4 to 6% of the whole milk, averaging about 5%, and constituting about 38% of the total solids.

587. Mineral Matter. When the whey is finally evaporated to dryness and the residue is heated to redness the ash or mineral matter remains. The mineral matter constitutes from 0.35 to 1.2% of the whole milk and is about 5% of the total solids. The mineral matter is composed chiefly of the phosphates and chlorides of sodium, potassium and calcium.

588. Contamination of Milk. Milk is one of the most easily contaminated substances. The contamination is due to minute organisms called *bacteria*, which are usually found in milk. It is not thought that the bacteria are in the milk before it is drawn from the cow, but dust from the stable or cow, dirty hands or milk vessels, are prolific sources of bacteria.

589. Nature of Bacteria. Bacteria are minute organisms of various shapes, such as circular, oval or rod shaped, capable of movement and of rapid growth in the proper medium. Many kinds of bacteria are useful and find practical application in soil fertility, yeast and vinegar manufacture, etc., but many of them are harmful. The food of bacteria is transformed into different compounds before it is eliminated, and if the bacteria capable of living in the body gain entrance, they multiply, and by consuming the tissues of the body produce disease. Fortunately comparatively few bacteria can do this, but as they are always present in the air and can thrive readily in milk the utmost precautions should be observed to avoid contamination.

590. Action of Bacteria on Milk. Lactic acid bacteria are the most active in milk. They act upon the milk sugar, changing it into lactic acid which makes the milk sour. As many as 20,000,000,000 may exist in a single pint of sour milk. Except for infants' use sour milk is not injurious and is often beneficial. Not all bacteria, however, are harmless. Such diseases as tuberculosis, from tubercular cattle, diphtheria, scarlet fever, dysentery, measles and smallpox from people suffering from the diseases, and typhoid fever from water used in the cans, may be transmitted by means of milk.

591. Pure Milk. In order to have pure milk it must be produced under sanitary conditions. There should be absolute cleanliness in and around the milking room, with plenty of light and air, free from dust. The cows should be clean, healthy and contented, and the men handling the cows and milk must be clean and well. All cans, bottles and caps should be thoroughly sterilized. Since the bacteria count in milk will average about eight times as many in summer as in winter when the milk is delivered to the customer, the milk should be placed in closed vessels, at as low a temperature as possible, as soon as drawn from the cow, and kept cold until used. It has been proposed to limit the number of bacteria to 500,000 per cubic centimeter, but this number is much too high for first class milk.

592. Grades of Milk and Special Milks. (1) *Modified Milk.* In modified milk, the milk is diluted, sugar and cream are added to bring them back to the normal percentage. This reduces the percentage of protein making it more easily digested by infants. Cows' milk is 3.8% protein, which is $\frac{1}{3}$ of the total solids. Meat and fish are richer in protein but $2\frac{1}{2}$ quarts of milk contain as much protein as one pound of meat, besides the fat and the sugar, and therefore, makes a better food, although it could not be used exclusively by adults, since it would not give a well balanced ration.

(2) *Skim Milk.* In cities it is illegal to sell skim milk, although it is relatively richer in protein and carbohydrates

than the whole milk. It is, therefore, generally sold as buttermilk, made by adding lactic acid bacteria to sour it, then adding sweet milk and churning. Skim milk usually contains about 10% of solids, one pound of the milk containing 0.034 pound of protein, and having a fuel value of 170, or one half that of whole milk.

(3) *Certified Milk*. The term, "certified milk" is applied to milk that shows a very low bacteria content, usually about 15,000 per cubic centimeter. These bacteria are not necessarily harmless, but are usually so. The milk is considerably higher in cost than the ordinary.

(4) *Sterilized Milk*. Heating the milk considerably above the boiling point kills the bacteria and the milk will remain sweet for a long time. The milk undergoes certain chemical changes, so that it is not suited for children and invalids. Boiled milk has a scum, probably due to the coagulation by heat of the protein, chiefly its albumen but possibly to a slight extent the casein also.

(5) *Pasteurized Milk*. Certain bacteria produce spores, similar in their general nature to seeds, and can resist great heat. Disease bacteria do not multiply in that manner, and hence can be killed at a lower temperature. If the milk is heated for about twenty minutes to a temperature of 165° F. or 74° C. the milk is made safe and will keep for a much longer time. It is, however, not exactly the same as the unheated milk.

(6) *Buddized Milk*. In this process the operation resembles pasteurization but the temperature is considerably lower, 50° C. or 122° F. and hydrogen peroxide is added. This is decomposed by the heat and the oxygen set free acts as a disinfectant killing the bacteria.

593. Preservatives in Milk. The common preservatives used in milk are salicylic acid, boric acid, borax and formaldehyde. While these are not active poisons they will, if taken regularly, affect the digestive system.

594. Adulteration of Milk. The adulteration of milk usually takes one of three forms (1) the addition of water;

(2) the removal of the fat without the addition of water; (3) the removal of the fat and the mixing of the skim milk with other milk, thus reducing the fat content of the latter. The specific gravity of whole milk varies from 1.029 to 1.033, while skim milk has a specific gravity of 1.033 to 1.037. Since the cream is lighter than the milk, water is added to bring down the specific gravity if the cream is removed. One quart of water weighs 2 pounds, $1\frac{1}{3}$ ounces, while one quart of milk weighs 2 pounds, $2\frac{1}{2}$ ounces. The specific gravity of the milk may be determined by the use of the lactometer.

595. Digestion of Milk. The *protein* of milk when used with other material is nearly all digested and in that respect resembles the protein of meats more nearly than it does that of vegetables, which may be $1/10$ to $1/4$ undigested. *Fats* in general, as found in milk, meats, eggs, butter and lard, are about 5% undigested. In vegetable foods the fat content is not as digestible nor is the fat of animal food as completely digested if the diet is composed of a great deal of fat. *Carbohydrates* are in general very digestible. Cane sugar is believed to be completely digested, and milk sugar is probably as digestible as the cane. Although animal foods contain more *protein* than milk, and the animal protein is more digestible, milk ranks among the most digestible foods, taking into account all of its components. It should not be taken alone nor in large quantities, because the pepsin and the acid of the gastric juice cause the casein to gather in large lumps. This does not happen to as great an extent if the milk is boiled or if lime water is added, since the latter neutralizes the acid and seems to retard coagulation. Milk is generally considered to be a healthful food, but some are made ill by drinking it.

596. Artificial Milk may be made from soy beans, which are first extracted with acid and then alkali is added slowly in excess. They are next ground in water containing alkalies and phosphates if desired. The strained liquid is sterilized and sugar

and emulsified vegetable fats are added. Sometimes hydrogen peroxide and potassium permanganate are added with the acid for oxidation.

597. Meat. Lean meat contains about 25% protein, 75% water with small amounts of fats, carbohydrates and mineral matter. Protein is necessary for building up and nourishing the protoplasm, or living cells of the body. Animal protein is more easily digested and assimilated than vegetable protein. If meat is eaten with potatoes—starch—we have all of the constituents of a complete diet. It is well known that the decomposition products of protein are not easily eliminated from the system so that an excess of meat should be avoided. On an average one-half pound of lean meat will furnish all of the protein necessary for an adult. Chemically, all meats are about the same, but there is a wide variety in flavor and digestibility.

598. Sound Meat should be firm and elastic, red in color and should hardly moisten the finger. It should be almost free from odor. It should give an acid reaction with litmus, and when dried at 100°C. should not lose more than 70 to 74 % of its weight.

599. Unwholesome Meat. There are a variety of ways in which meat may become unwholesome. It may contain disease bacteria, such as tuberculosis or trichina. If the animal is slaughtered too young, or if it died a natural death, or if insanitary methods of killing and handling are followed the meat is not suitable for food.

Pale pink meat indicates that the animal was diseased.

Dark purple meat indicates that the animal died a natural death.

600. Preserving Meats. Meat is best preserved by cooling it to -9°C . freezing it solid. Chemical preservatives, such as borax, boric acid, sulphurous acid, benzoic acid, etc., are used at times but are considered adulterants, because they are added to deceive. Sulphurous acid is used to give a bright red color. It is added in the form of the sodium or calcium salt to sausage

and other ground meat. Salt, wood smoke and potassium nitrate, long used in curing hams, dried beef, corned beef etc., are well known, and because of long usage are not considered adulterants.

601. Gelatin. Gelatin is a nitrogenous substance having a formula said to be $C_{102}H_{151}N_{131}O_{39}$ forming a jelly with 50 times its weight of water. It is extracted from horns, tendons, hides and hoofs, and is practically a very pure glue. The animal substances are first treated with lime, and washed, and the gelatin is then extracted with hot water. If white gelatin is wanted, it is bleached with sulphurous acid. The gelatin is then dried and powdered or sold in thin sheets. Gelatin is considered a wholesome food, but it must be kept dry or it decomposes. Boiling does not insure sterility as it may contain tetanus spores, which are not killed by boiling.

602. Eggs. The food value of eggs is found in the protein and fat. Small amounts of carbohydrates and mineral matter are also found, two-thirds of the carbohydrates being in the white. Eggs average about 8 to the pound, though there are wide variations. The whole egg averages about 11% shell, 32% yolk, and 57% white. Bantam eggs and eggs from hens for fattening usually contain a larger proportion of yolk. White shelled eggs contain a larger proportion of shell than brown. The following table shows the comparison between the different parts:—

	Percentage of					Calories per pound
	Refuse	Water	Protein	Fat	Ash	
Whole eggs	11	65 5	11 9	9 3	.9	635
Edible portion	0	73.7	13 4	10 5	1.	720
White only	0	86 2	12 3	.2	.6	250
Yolk only	0	49 5	15 7	33 3	1.1	1705

Duck, goose, turkey and guinea fowl eggs do not vary a great deal from these proportions.

603. Eggs and Other Foods. In general eggs more nearly resemble meat, milk and cheese than vegetable foods such as flour, potatoes, etc. There is very little difference in the composition of cooked and raw eggs, but there is a difference in the texture and, therefore, in the digestibility. There is a great difference in the composition of the white and the yolk. The fats of the latter are chiefly palmitin, olein and stearin, together with some phosphorus, besides other bodies more complex in structure, and small amounts of calcium, magnesium, potassium and iron salts. The albumen of the white contains sulphur, forming silver sulphide on silver, or hydrogen sulphide if the albumen decomposes. The flavor of eggs is due largely to the food given the hens. Eggs are quite thoroughly digested, whether cooked or raw, the chief difference being in the length of time required.

604. Storage and Preservation of Eggs. The shell of eggs is of no use as food. It is composed of calcium carbonate, 93.7%; magnesium carbonate, 1.3%; tricalcium phosphate, 0.8%; and organic matter, 4.2%. The shell of an egg is porous and micro-organisms gain access through the pores.

Cold storage. If eggs are placed in cold storage at 31° to 34° F. they keep better after removal than if stored at 30° F. Eggs stored at 35° to 40° F. keep better and have a finer flavor. Packing eggs in various powders and liquids is widely used but for the best results a 10% solution of sodium silicate (water glass) may be used, one gallon of water glass being sufficient for 50 dozen eggs. The solution should not be strongly alkaline, and should be made with boiled, cooled water. The eggs should be clean but not washed and after the solution is poured over them they should be set in a cool place.

Egg powders often contain no eggs; the chief ingredient being baking powder containing rice starch. Egg powder containing egg may be made from rice starch 90% and dried egg 10%.

605. Vitamines. The most startling discovery in relation to food and nutrition made in modern times relates to certain

subtle substances to which the name "vitamines" has been given. These substances are found in foods in such minute quantities that they have so far escaped chemical analysis, but their properties have been accurately determined by experiments upon animals and observations upon large numbers of human beings, and knowledge concerning them has come to hold a very important place in the science of nutrition.

While vitamins do not enter into the composition of the body, they are absolutely essential to health and life. If any one of them is lacking, or is deficient in the food, the body languishes. Three different vitamins are known—fat-soluble A, water-soluble B and water-soluble C. Vitamins A and B resist the action of heat; C may be influenced by heat, depending upon conditions.

Fat-soluble A is highly necessary to promote the growth of young animals. In its absence rickets appears in the young, also a disease of the eyes in children, and night blindness in adults. This vitamin is found in butter, cream and other dairy products. Egg yolk and cod liver oil contain it, but it is not found in many other oils. It is also found in great abundance in greens of all sorts. A sufficiency of this vitamin is secured by the use of butter, cream and greens. Lack of vitamin A increase susceptibility to infection.

Water-soluble B is one of the most important of all the vitamins from a dietetic standpoint, for the reason that it is absolutely essential for growth and development of the young. This vitamin is likely to be deficient in foodstuffs. In cereals it is found only in the bran, and consequently in fine flour, polished rice, new process cornmeal, and most breakfast foods it is almost entirely lacking. An abundance of this vitamin is necessary to maintain the nerves in a healthy state. When it is absent or deficient, loss of weight and various nervous symptoms appear, particularly neuritis, and if not arrested, the disease may steadily advance to paralysis and death. On this account it is known as the anti-neuritic vitamin. In countries

where polished rice is used as an almost exclusive food, the fatal disease known as beri-beri is very common. Wheat bran contains this vitamine in great abundance. It is also found most abundantly in yeast and yeast extracts. Since vitamine B is not readily stored in the body care must be exerted to maintain a constant supply of foods containing it.

Water-soluble C is found in fresh fruit and vegetables, particularly in the citrous fruits, turnips, cabbage, potatoes and tomatoes. Since this vitamine may be destroyed by cooking, the importance of using some fresh, uncooked foods daily is readily seen. In an acid medium vitamine C remains stable when heated.

It is probable that if food in sufficient amounts and variety is taken regularly no special preparations containing vitamines are necessary.

606. Digestion of Foods. *Action of the Saliva.* The secretions of the digestive glands owe their power of dissolving nutrients to certain complicated chemical compounds known as enzymes. The mixed saliva is slightly alkaline; when pure it is chiefly water and an enzyme called ptyalin. It acts upon the starch to a limited extent, changing it into sugar which is soluble in the water of the saliva; the action is better on cooked than on raw starch. The chemical action as it occurs, may be represented by the equation



($\text{C}_6\text{H}_{10}\text{O}_5$ is maltose.) There is comparatively little action on starch in the mouth, for the saliva aids chiefly in swallowing and in producing the sensation of taste.

607. In the Stomach the gastric juice acts upon the food that has been swallowed. The gastric juice consists mainly of water, holding a solution of about 0.2% of hydrochloric acid and two enzymes called pepsin and rennin. Hydrochloric acid neutralizes the alkaline saliva and stops its action on the starch. Normally about three quarts of gastric juice will be produced in

twenty-four hours, making about 6 cc. of absolute hydrochloric acid. The action of the pepsin is to change the proteins to soluble peptone. Pepsin acts only in an acid medium, so that the hydrochloric acid is necessary. Peptones are probably produced simply for absorption purposes, since they are not found in the blood, and when introduced act as a poison. Rennin acts on protein of milk, causing it to coagulate as casein, thus separating it from the rest of the milk, so that the pepsin can act upon it.

The hydrochloric acid, besides helping the pepsin, destroys the germs of fermentation and disease and probably dissolves mineral salts, in addition to separating protein from fats and starches. The heat of the stomach liquefies the fats and the liquid portions aid in dissolving sugar. The mixture, and all these substances in the stomach, gives a milky acid called chyme, which from time to time is forced into the small intestine.

608. In the Small Intestine are three digestive fluids—the pancreatic juice from the pancreas, the bile from the liver and the intestinal juice; these are all alkaline and change the acid chyme into alkaline chyle. The pancreatic juice from the pancreas has three enzymes: trypsin, amylapsin and steapsin. The trypsin is more powerful than the pepsin and acts in an alkaline medium, although it may act in a neutral or slightly acid medium. This acts upon the protein changing it to soluble peptones, but the change is not accompanied by swelling, as when the pepsin acts upon proteins. The peptones are here prepared for absorption. The amylapsin digests the starch, and both in structure and action is practically like the ptyalin of the saliva. The steapsin or lipase acts upon fats, producing saponification and emulsifying the fats. In saponification the fat is first split into glycerin and fatty acids, the latter unites with alkalis and alkaline salts to form soluble soaps. In emulsifying, the fat is separated into tiny droplets surrounded by the fatty acid or alkaline material, preventing a recombination

until after absorption, when the droplets recombine to form the body fats.

The bile increases the emulsifying power of the steapsin and aids in splitting the fats. It may help to prevent putrefaction and helps to neutralize the acid of the chyme, causing the precipitation and separation of the proteins, so that the trypsin can act.

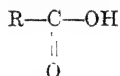
The intestinal juice, coming from the crypts of Lieberkuhn, is a yellowish liquid, with a strong alkaline reaction, which is derived from sodium carbonate. This aids in emulsifying the fats. There is only a small amount in the upper part of the intestine, but it is very abundant in the lower region. It has two enzymes, one similar to amyllopsin, which aids in converting the starch into sugar; the other, invertin, converts the cane sugar and other forms of sugar into grape sugar for absorption.

There are *no digestive juices secreted in the large intestine*, and any digestion that may occur there, is caused by the digestive juices coming through, with the food, from the small intestine. The indigestible substances, such as elastic tissue, cellulose, mucin, and various other substances that are of no value in nutrition, then pass from the system.

CHAPTER XXVI

ACIDS, ESTERS, WATER AND ASH

609. Although there are a *great many organic acids*, only a few are of special importance in elementary food chemistry. Before beginning the study of this chapter the student should review §§270-280, in Chapter 12. There it will be seen that the general formula for monobasic organic acids is



They may be formed by the oxidation of an aldehyde, the aldehyde being formed by the oxidation of an alcohol. The acids differ from the corresponding hydrocarbon by having two oxygen atoms in place of two hydrogen atoms. The relations between the hydrocarbons, alcohols, aldehydes and acids may be seen from the following table which shows the empirical formulas of the simplest members of the marsh-gas series:

<i>Hydrocarbon</i>	<i>Alcohol</i>	<i>Aldehyde</i>	<i>Acid</i>
Methane, CH ₄	Methyl, CH ₄ O	Formic, CH ₂ O	Formic, CH ₂ O ₂
Ethane, C ₂ H ₆	Ethyl, C ₂ H ₆ O	Acetic, C ₂ H ₄ O	Acetic, C ₂ H ₄ O ₂ , etc.

In like manner the other members of the series form corresponding acids, etc. These acids are known as the fatty acids. The lower members are more strongly acid and are more soluble in water, while the higher members are tasteless solids which melt to form oily liquids only slightly acid.

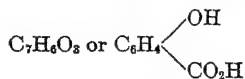
610. Acetic Acid, CH₃CO₂H, or ethanoic acid, may be prepared by the oxidation of ethyl alcohol or by the destructive distillation of wood. Impure acetic acid is sometimes called pyroligneous acid. The acid prepared in either way must be purified by passing through charcoal, distilling and freezing which is repeated until a pure acid is obtained.

Acetic acid is a clear, colorless liquid that boils at 120° . It solidifies at 16.7° and is known as glacial acetic acid. Its specific gravity is 1.055 at 15° and increases when water is added until it reaches 1.075, which gives an acid of about 80 per cent. The specific gravity then decreases if more water is added until an acid of 43 per cent is reached which has the same specific gravity as the pure acid. Glacial acetic acid is a very pure acid, occurring as colorless crystals at ordinary cool temperatures, but melting to a colorless liquid in a moderately warm room. Acetic acid is used extensively in a dilute and usually impure form as vinegar which contains from two to six per cent of the acid. Vinegar made from cider usually contains many small eel-like organisms which are the larvae of a small fly found near apples and other fruits.

Elaborate experiments carried out concerning the action of different chemicals upon vinegar eels show that they resist the action of almost all chemicals supposedly fatal to lower forms of life in a most remarkable manner and that they live for a month or more in some solutions fatal to man.

611. Of the Other Fatty Acids but little need be said. *Butyric* acid, $C_3H_7CO_2H$, is found in rancid butter; *oenanthylic* acid, $C_8H_{13}CO_2H$, in butter; *caprylic* acid, $C_7H_{15}CO_2H$, in butter and cheese; *capric* acid, $C_9H_{19}CO_2H$, in limburger cheese; *palmitic* acid, $C_{15}H_{31}CO_2H$, in butter and tallow; *stearic* acid, $C_{17}H_{35}CO_2H$, in tallow and lard; *medullic* acid, $C_{20}H_{41}CO_2H$, in ox marrow and beef fat; *cerotic* acid, $C_{26}H_{53}CO_2H$, in beeswax, etc. The boiling point of the normal acids gradually rises.

612. In the Aromatic Series of Hydroxy Acids, $C_nH_{3n-6}O_3$, one of the best known is *salicylic* acid,



also known as ortho-hydroxy-benzoic acid.

Salicylic Acid forms needles that melt at 156° . It is a powerful antiseptic, resembling phenic acid, but is without the disagree-

able odor and highly poisonous nature of the phenic acid. It is used as an antiseptic in foods, etc., and is objectionable not so much on account of its poisonous nature as its interference with the digestion. When heated salicylic acid decomposes into phenic acid and carbon dioxide. A solution of salicylic acid gives a deep blue or violet color when ferric chloride solution is added. This serves as a test for the acid. Among the salts of salicylic acid may be noticed sodium salicylate which is used as a remedy for rheumatism and appendicitis.

The other acids common in foods belong to different organic series, but the different structural formulas will not be given.

613. Tartaric Acid or dihydroxysuccinic acid, $C_4H_6O_6$ or $(CHOH)_2(CO_2H)_2$, occurs widely distributed in fruits, sometimes free and sometimes combined as potassium or calcium tartrate. Tartaric acid may be made by oxidizing sugar of milk with nitric acid or by oxidizing cane sugar, starch, glucose, etc. It may be prepared from "argol" which is the impure potassium acid tartrate deposited in wine casks. The argol is first treated with chalk to form the calcium salt and then with sulphuric acid. The ordinary tartaric acid crystallizes in large monoclinic prisms, easily soluble in water and alcohol.

614. Citric Acid $C_6H_8O_7 \cdot H_2O$ is found in such fruits as lemons, currants, raspberries, gooseberries, etc. The acid is prepared from lemon juice by treating with lime and sulphuric acid. The yield is about 5.5 per cent. Citric acid crystallizes in rhombic prisms easily soluble in water. The salts of citric acid are citrates of which there are three varieties, depending upon the number of hydrogen atoms replaced by the metal, there being three that are replaceable.

615. Gallic Acid, $C_7H_6O_5$ occurs in sumac, Chinese tea, etc. It may be prepared by boiling tannin or tannic acid with dilute sulphuric acid. It is soluble in water and when ferric chloride is added gives a blue-black precipitate which dissolves in excess to a dark green solution.

616. Tannic Acid, $C_{14}H_{10}O_9$, occurs in gall nuts, oak bark, tea leaves, etc. It is an amorphous powder soluble in water. When ferric chloride is added iron tannate is formed and is blue-black in color. Tannic acid is used in making ink and in tanning.

ESTERS

617. Esters are derivatives of acids in which the hydrogen of the carboxyl group, CO_2H , has been replaced by some hydrocarbon radical, such as CH_3 , C_2H_5 , C_6H_5 , etc. Thus acetic acid has the formula CH_3CO_2H , while the formula for ethyl acetate is $CH_3CO_2C_2H_5$. Here it may be seen that the ethyl radical, C_2H_5 , has replaced the last H in the formula for the acid.

In the earlier developments of organic chemistry the esters were commonly spoken of as "compound ethers," and the names "acetic ether," "methylsalicylic ether," etc., are still occasionally employed.

In structure the esters are salts of the acids, and it is often convenient to name them in that manner, but they differ from acids very greatly in the degree of ionization, salts ionizing to a high degree and reacting rapidly, while esters ionize very slightly and react slowly.

Many esters are formed in the various fruits that are commonly used. They are also made in the laboratory and are used very extensively in the preparation of artificial fruit flavors for soda fountains, etc. The following table shows how some of the best known artificial flavors are prepared commercially:

10 grams of the food to be examined. It is then heated in a weighed dish on a water bath for several hours, cooled and weighed. It should then be heated again for about 45 minutes, cooled and weighed; and the process repeated until two consecutive weights are the same.

MINERAL MATTER

620. Varying amounts of mineral matter are found in nearly all foods. Some, such as lard, olive oil, cane sugar, etc., contain no mineral matter. When food is thoroughly burned, after drying and charring, the white, insoluble ash represents the mineral matter. The common mineral substances found in foods, and the average amount required per day by an adult are shown in the following table:

	<i>grams</i>
Phosphoric acid, P_2O_5	3 to 4
Sulphuric acid as SO_3	2 to 3.5
Potassium oxide, K_2O	2 to 3
Sodium oxide, Na_2O	4 to 6
Calcium oxide, CaO	0.7 to 1.0
Magnesium oxide, MgO	0.3 to 0.5
Iron, Fe	0.006 to 0.012
Chlorine, Cl.	6 to 8

621. Charts prepared by C. F. Langworthy, and published by the United States Department of Agriculture, show the various constants of different food materials as seen in the following table:

<i>Name of the food material</i>	<i>Protein</i>	<i>Fat</i>	<i>Carbohydrates</i>	<i>Ash</i>	<i>Water</i>	<i>Fuel value in calories per lb.</i>
Apple	0 4	0 5	14 2	0 3	84 6	290
Bacon	9 4	67 4		4 4	18 8	3030
Beef suet	4 7	81 8		0 3	13 2	3510
Butter	1 0	85 0		3 0	11 0	3410
Buckwheat.	10 0	2 2	73 2	2 0	12 6	1600
Beefsteak	18 6	18 5		1 0	61 9	1130
Buttermilk	3 0	0 5	4 8	0 7	91 0	160
Bean, fresh shelled	9 4	0 6	29 1	2 0	58 9	740
Bean, green string	2 3	0 3	7 4	0 8	89 2	195
Bean, navy dry	22 5	1 8	59 6	3 5	12 6	1600
Banana	1 3	0 6	22 0	0 8	75 3	460
Codfish, fresh	12 8	0 4		1 2	82 6	325
Codfish, salt	21 5	0 3		24 7	53 5	410
Corn, dried	10 0	4 3	73 4	1 5	10 8	1800
Corn, green	3 1	1 1	19 7	0 7	75 4	500
Corn bread	7 9	4 7	46 3	2 2	38 9	1205
Cream cheese	25 9	33 7	2 4	3 8	34 2	1950
Cottage cheese	20 9	1 0	4 3	1 8	72 0	510
Cream	2 5	18 5	4 5	0 5	74 0	865
Candy stick			96 5	0 5	3 0	1785
Celery	1 1		3 4	1 0	94 5	85
Chestnut	10 7	7 0	74 2	2 2	5 9	1875
Cocoonut, dried	6 3	57 4	31 5	1 3	3 5	3125
Dried beef	30 0	6 6		9 1	54 3	840
Egg, whole	14 8	10 5		1 0	73 7	700
Egg, white	13 0	0 2		0 6	86 2	265
Egg, yolk	16 1	33 3		1 1	49 5	1608
Fig, dried	4 3	0 3	74 2	2 4	18 8	1475
Fruit, canned	1 1	0 1	21 1	0 5	77 2	415
Grapes	1 3	1 6	19 2	0 5	77 4	450
Grape juice, unfermented	0 2		7 4	0 2	92 2	150
Herring, smoked	36 4	15 8		13 2	34 6	1355
Honey	0 4		81 2	0 2	18 2	1520
Jelly, fruit			78 3	0 7	21 0	1455
Lard		100 0				4080

<i>Name of the food material</i>	<i>Protein</i>	<i>Fat</i>	<i>Carbohy- drates</i>	<i>Ash</i>	<i>Water</i>	<i>Fuel value in calories per lb</i>
Lamb chop	17 6	28 3		1 0	53 1	1540
Mackerel	18 3	7 1		1 2	73 4	645
Macaroni	3 0	1 5	15 8	1 3	78 4	415
Milk, whole	3 3	4 0	5 0	0 7	87 0	310
Milk, skimmed	3 4	0 3	5 1	0 7	90 5	165
Molasses	2 4		69 3	3 2	25 1	1290
Oat	11 8	5 0	69 2	3 0	11 0	1720
Olive oil		100 0				4080
Oyster	6 2	1 2	3 7	2 0	86 9	235
Onion	1 6	0 3	9 9	0 6	87 6	225
Pork chop	16 9	30 1		1 0	52 0	1580
Parsnip	1 6	0 5	13 5	1 4	83 0	230
Potato	2 2	0 1	18 4	1 0	78 3	385
Peanut	25 8	38 6	22 4	2 0	9 2	2500
Peanut butter	29 3	46 5	17 1	5 0	2 1	2825
Rye	12 2	1 5	73 9	1 9	10 5	1750
Rice	8 0	2 0	77 0	1 0	12 0	1720
Rolled oats, cooked	2 8	0 5	11 5	0 7	84 5	285
Raisins	2 6	3 3	76 1	3 4	14 6	1605
Smoked ham	16 1	38 8		4 8	40 3	1940
Sugar granulated			100 0			1860
Sugar, maple			82 8	0 9	16 3	1540
Strawberry	1 0	0 6	7 4	0 6	90 4	180
Toasted bread	11 5	1 6	61 2	1 7	24 0	1420
Wheat	12 2	1 7	73 7	1 8	10 6	1750
White bread	9 2	1 3	53 1	1 1	35 3	1215
Whole wheat bread	9 7	0 9	49 7	1 3	38 4	1140
Walnut	16 6	63 4	16 1	1 4	2 5	3285

622. The following table shows a brief list of some of the foods that are rich in iron, phosphorus and calcium, showing the percentages of iron, phosphorus pentoxide and calcium oxide:

<i>Foods Rich in Iron</i>		<i>Foods Rich in Phosphorus</i>		<i>Foods Rich in Calcium</i>	
Beans, dried . . .	0070	Cheese	1 45	Cheese	1.1
Peas, dried . . .	0056	Beans, dried . . .	1 14	Figs290
Wheat entire . . .	0053	Cocoa . . .	1 10	Cauliflower17
Beef, lean	0038	Peas, dried . . .	91	Milk168
Oatmeal	0036	Wheat . . .	902	Cocoa14
Figs, dried	0032	Chocolate . . .	90	Peas, dried14
Spinach	0032	Oatmeal . . .	872	Oatmeal13
Eggs	0030	Walnuts . . .	77	Walnuts108
Dates	0030	Chicken . . .	58	Celery10
Prunes	0029	Beef50	Dates10
Cocoa0024	Pork45	Eggs093
Walnuts	0021	Halibut . . .	40	Spinach090
Peas, fresh	0016	Bread, whole wheat	40	Turnips089
Bread, whole wheat . .	0015	Eggs . . .	37	Carrots077
Grapes	0013	Figs . . .	332	Cabbage068
Potatoes	0013	Peas, fresh . . .	26	Wheat061
Cabbage	0011	Prunes . . .	25	Oranges06
Lettuce	0010	Corn, sweet . . .	22	Prunes06
Asparagus0010	Bread, white20	Lemons05
Rice	0009	Potatoes . . .	14	Lettuce05
		Cauliflower14		

CHAPTER XXVII

FLOUR, BREAD, LEAVENING AGENTS, SPICES, FLAVOR- ING EXTRACTS AND BEVERAGES

623. Importance of Wheat in the Diet. In the course of 400 dietary studies made by the Office of Experiment Stations it has been found that wheat flour and other wheat products supply 20% of the total food used in the United States, and that this constitutes 30% of the total protein, 5% of the total fats, and 42% of the total carbohydrates.

624. Flours From Other Grains. Corn, rye, barley, oats, rice, millet, etc., are also used as flour or meal in varying amounts, but in the United States wheat flour is the most important in bread making, and as they are all very similar, a study of wheat will enable the student to understand the principles of production from the other varieties. As a class cereals contain about 10% of protein, 60 to 80% of carbohydrates and a small proportion of fats and mineral matter.

625. The Wheat Kernel. A kernel of wheat is a small, oval seed, consisting largely of starch cells and gluten forming protein, surrounded by six layers, the inner one—the cereal or aleurone layer—forming with the starch cells the endosperm. (Fig. 153.)

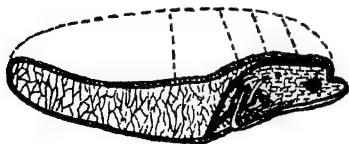


FIG. 153 Wheat Structure.

The starch is in the form of grains, embedded in a network of protoplasmic material, several hundred grains forming a starch cell, while 10,000,000 to 20,000,000 grains are found in a single kernel of wheat.

The aleurone layer constitutes about 8% of the entire weight of the kernel. Surrounding the aleurone layer are five layers known as bran, constituting about 5% of the entire kernel.

The outer three layers of the bran are called the skin; the fourth contains the greater part of the coloring matter, and is called the testa; the fifth is a thin membrane separating the testa and the aleurone layer. At the lower end of the grain, almost surrounded by the endosperm, is the embryo or germ, whose cells contain a large proportion of fat. The cellulose is more abundant and more woody in the outer parts of the grain and is less digestible than the softer inner portions.

626. Grinding. In modern, high roller grinding, the grain is screened, cleaned and treated with heat and moisture, called tempering, so that the bran may be entirely removed at one grinding. The bran is removed and the stock is then run through five or six pairs of rollers, each pair set a little nearer together than the last. Each grinding is called a "break." After each "break" the fine flour is sifted out and the leavings, known as "middlings," are ground and sifted several times. Careful millers grind as near the aleurone layer as possible and leave as much of the germ in the flour as is consistent with good color.

627. Grades of Flour. There are numerous grades of flour but those generally recognized are "patent," "clear," "straight," and "red dog," the patent and clear being often divided into first and second quality.

Patent Flour is the best flour obtainable, and is made from the purified middlings of the first break, varying from 55 to 75% of the entire wheat, and averaging about 65%. It contains the smallest percentage of ash—about 0.42 to 0.43%. Bleached straight or clear flour may raise the percentage of the so-called patent to 85 or 90% of the entire grain.

Clear Flour, consisting of a mixture of odds and ends, and while usually made from low grade middlings and breaks, frequently contains the finest quality of middling stock from the tail of the mill. It constitutes 15 to 30% of the entire grain, averaging 25 to 27%. The ash content varies from 0.80 to 1.75%.

Straight Flour contains all of the wheat fit for human consumption, red dog being usually omitted. Straight flour averages 0.50% ash. It may be a mixture of patent and first clear. It is harder to ferment, takes longer, and makes a runny dough, yielding a coarse undeveloped loaf with a coarse, dry, hard, tough crust.

Red Dog constitutes from 3 to 5% of the entire grain. It is about 3.5% ash and is essentially a stock food.

Graham Flour is really wheat meal containing all of the grain. The wheat is cleaned and ground between a single set of rollers. Its ash content is about 1.72%.

Whole Wheat Flour or entire wheat flour, is often made by removing part of the bran and grinding the remainder, but much of it is said to be a mixture of patent, middling and low grade flours, with considerable of the germ. It is finer than graham, but not as fine as white flours. The ash varies from 1.02 to 1.60%.

Blended Flours. If two grades of flour, or better, two grades of wheat are mixed before grinding, the resulting flour is called a blend.

628. Grades of Wheat. Wheat varies considerably in quality for making flour, depending upon several factors—the soil, climatic conditions, and kind of seed being the most important causes of variation.

Hard Wheat is rich in gluten of a strong tenacious character, while *soft wheat* contains less gluten and proportionately more starch. Wheat sowed in the fall is known as winter wheat, while that sowed in the spring is called spring wheat, giving rise to further varieties, depending upon the place where the wheat is grown, as *Minnesota hard Scotch Fife spring wheat*, *Oklahoma hard winter wheat*, *Oregon soft winter wheat*, etc.

Durum Wheats, introduced from Russia, are spring wheats, closely related to the common varieties, but differing in the size and the character of the plant and grain. The grains are larger, and as the name indicates, are very hard. The grains are clear

amber in color instead of being reddish, like the common winter and spring varieties. It grows rapidly and vigorously, resists drouth and disease, and matures early. About 87.5% of the durum wheat grown in the United States comes from North and South Dakota; about 7% from Minnesota and the rest from scattered localities through the West. The durum wheats have a more crude protein, and make a stickier dough, harder to handle; but the dough holds moisture better, and having a greater absorptive power, yields more loaves to the barrel than the common varieties.

Hard and Soft Wheats. The gluten of all hard wheats will take a larger proportion of water and will make larger loaves, but the bread made from soft wheats is usually considered to have a finer flavor. Flours are classed as "strong" or "weak" according to their proportion of gluten.

629. Wheat Gluten. The gluten of wheat is not a simple protein compound but contains glutenin and gliadin. In different flours the proportion of gluten varies and also the proportion of the glutenin to the gliadin in the gluten. The gliadin is a sort of plant gelatin which binds the flour particles together in the dough, giving it tenacity and adhesiveness. The glutenin is the material to which the gliadin adheres. If the gliadin is in excess the dough is soft and sticky; if deficient in quantity, it lacks the power to expand.

630. Relation of Gluten and Starch. Extensive experiments carried on at the Minnesota Experiment Station indicate (1), that it is the gluten, rather than the starch content, that determines the bread making power of flour; (2) that an abnormally large amount of gluten does not yield a correspondingly large loaf; (3) that if the gliadin was removed, either in whole or in part, the dough was not sticky, but felt like putty, and broke in the same way. The loaf, when placed in the oven, at first expanded a little, then broke and decreased in size. When baked it was about half the size of a loaf made from an equal

amount of normal flour and was decidedly inferior. It was about as heavy as an equal volume of rubber.

631. Bread. Bread contains all of the substances used as food but is deficient in fat, hence the logical use of butter. It digests slowly, and is therefore satisfying. Bread contains only a few ingredients, but the chemical processes involved are long and complicated. Essentially bread is composed of flour and water, or potato water, a little salt, with or without a leavening agent, usually using two or three parts of flour to one of water. For fancy varieties, other ingredients are added, such as eggs, sugar, cinnamon, nuts, raisins, currants, etc.

Straight Dough, or offhand dough, is made by mixing all of the ingredients at one time, then setting the mass in a warm place to rise for ten hours or more before baking. It requires more yeast and a stronger flour, and needs a longer time to rise, but gives an unusually large yield in bread.

Sponge Dough is made by stirring yeast and a little strong flour into water or potato water, setting the mixture in a warm place to rise for eight or ten hours, then thoroughly mixing the sponge with the remainder of the flour, which may be a weaker flour than that used in the sponge, since no great pressure will come upon the gluten. Salt is added near the end of the mixing to check any lactic or butyric fermentations that may occur. It also improves the flavor of the bread, and exerts a toughening and binding effect upon the gluten. Sponge dough requires two short kneadings in soft dough, instead of one long one in stiff dough, and the bread has better keeping qualities. After the second kneading the bread is made into loaves, allowed to rise until practically double the original size, and then baked.

632. Baking. The heat of the oven should not be too great, especially at first or the crust will harden too quickly and the interior will not be baked before the crust is thick and dark, and the latter will be lifted up by the expanding gas forming great holes. Too rapid formation of the crust may be prevented by moistening the tops of the loaves, or by spread

ing a little butter over the top of the loaf. For ordinary purposes the temperature should be from 205° to 260° C. (400° to 500° F.). For large loaves the temperature should be lower than for small ones to insure the baking of the inner portions before the crust is too hard. Bread dough expands because of the formation of carbon dioxide in the dough, either from the action of yeast upon the soluble carbohydrates of the dough, or by the action of baking powder.

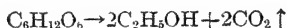
633. Wild Yeast and its Action. If fresh bread dough is allowed to stand in the air for a considerable time yeast cells will fall into it from the air and eventually cause it to sour and rise. If a little of this sour dough is kept and added to the next batch of fresh bread, the action is rapid. The process may thus be made continuous, but it is not used except for black bread, yeast being preferred for white.

634. Fermentation may be produced by yeast, or by enzymes. The latter are not living organisms but are produced by living organisms. Saliva contains an enzyme called ptyalin. When mixed with food it changes starch into a form of sugar, making it more easily digested. Hence the necessity of thorough mastication. In grains is an enzyme, called diastase, capable of producing a similar effect upon starch in much larger quantities. Malt is made by sprouting moistened barley, and the diastase of the malt can change more starch into sugar and dextrin than is contained in the malt, so one part of malt is added to five parts of boiled, mashed rye or barley and all of the starch in both grain and malt is changed. This mixture of malt and mash is known as wort.

635. Action of Yeast on Wort. Some yeast is then added to the wort and the temperature is kept at 30° C. Much new yeast is formed and is carried to the top by a stream of carbon dioxide. The yeast is skimmed off and passed through a hair sieve floating in water in a barrel. The impurities remain in the water, and the yeast gradually settles to the bottom. The water is changed several times until at last the yeast is like a muddy

deposit. Since it is hard to separate the yeast from the water starch is often added to absorb the water and the mixture is made into cakes and sold as compressed yeast. Dry yeast, compressed in modern presses, contains no starch.

636. Action of Yeast on Sugar. When the yeast acts upon sugar, alcoholic fermentation is produced and carbon dioxide is formed.



The sugar is found in and is produced from the starchy material of the flour. The carbohydrates of the flour are about 1% sucrose, and a little raffinose, which are converted into dextrose by the enzyme, invertase, in the yeast before fermentation. In time enough alcohol is formed to kill the yeast plant, which is a small round or oval body, reproducing either by budding or by spores. (See Fig. 154.) Sugar is consumed and the presence of oxygen and nitrogen seems to give the best development to the plant. In the growth of yeast cells the buds cling to the parent for a short time and then separate and become parents in turn.

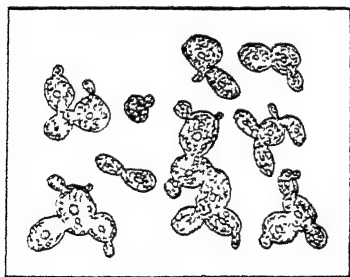


FIG. 154 Yeast, Showing Budding

Under favorable conditions each forms a new cell once in about twenty minutes. A single cell of yeast separated from all other organisms and allowed to grow in complete isolation, will yield a yeast having all the characteristics of the original yeast, and is known as a pure culture yeast. After alcoholic fermentation ceases

in the bread, lactic and butyric fermentations are apt to occur. Salt stops fermentation, and it is therefore added to the bread, but not until near the end of the kneading, otherwise the alcoholic fermentation will stop too soon.

Tooth paste or powder containing yeast is now on the market. It contains about 45% of yeast.

637. Baking Powder. If baking powder is used no alcohol is formed in the bread, but carbon dioxide and certain salts are produced. The action of the carbon dioxide in raising the bread is the same whether it is obtained from alcoholic fermentation or from baking powder, but the taste of the bread is different. Baking powder consists usually of sodium bicarbonate mixed with an acid, or an acid salt, which decomposes the bicarbonate in the presence of water, setting carbon dioxide free.

638. Classification of Baking Powders. Baking powders are divided into several classes, according to the kind of acid or acid salt used to decompose the bicarbonate.

Tartrate Powders use either potassium bitartrate, $\text{KHC}_4\text{H}_4\text{O}_6$, or tartaric acid, $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$.

Phosphate Powders use sodium acid phosphate, Na_2HPO_4 , potassium acid phosphate, K_2HPO_4 , or calcium acid phosphate, CaHPO_4 .

Alum Powders use some form of alum. By using alum the bread is made whiter, but as alum is considered a harmful ingredient owing to its poisonous properties, its use is prohibited in some states. If used at all, potassium alum is not as objectionable as the cheaper ammonium and sodium alums.

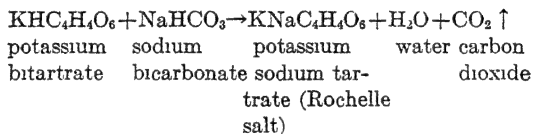
Tartrate and Phosphate Powders are not objectionable, except that with potassium bitartrate the reaction with sodium bicarbonate produces potassium sodium tartrate, $\text{KNaC}_4\text{H}_4\text{O}_6$, commonly called Rochelle salt or Siegnette salt, which acts as a laxative. There are some advantages in using potassium bitartrate instead of tartaric acid, since the former is less soluble in cold water. The carbon dioxide is, therefore, formed more slowly and the dough can be kept longer. The tartrate powders show no tendency to darken the bread as is the case when the different acid phosphates are used, though otherwise these are very good substitutes for the tartrates.

Magnesium carbonate, MgCO_3 , is sometimes used instead of

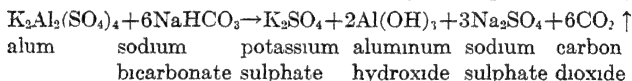
sodium bicarbonate. Ammonium carbonate, $(\text{NH}_4)_2\text{CO}_3$, is also used in very light pastry, but it requires expert handling and is but little used.

A *Drying Agent*, such as starch, or some kind of flour, is usually added to absorb any moisture that would otherwise cause a reaction and waste materials.

639. The Chemical Action of Baking Powders. The following equation shows the chemical reaction when potassium bitartrate is used with baking soda.

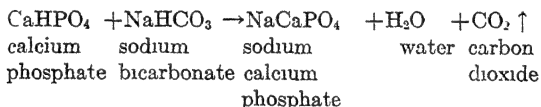


When alum is used the reaction may be represented by

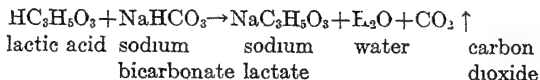


Sodium or ammonium alums are usually substituted because they are cheaper.

When calcium phosphate is used the residue is sodium calcium phosphate:



Sour milk, which contains lactic acid, $\text{HC}_3\text{H}_5\text{O}_3$, also reacts with sodium bicarbonate. It is frequently used and the equation for the reaction is



For the best results in baking at least 3.5 grams of carbon dioxide should be liberated for each kilogram of flour used.

Calcium carbonate should be used in baking powder only when no other calcium salts are used. Free sulphuric acid should not test more than 0.1%. If the baking powder is alkaline the alkalinity should not be more than 1%. Mineral fillers must not be used.

640. The following table shows the composition of several baking powders:

Baking Powder Sample	Acid Material					Source of Carbon Dioxide			Drying Agent			
	Tartaric Acid	Potassium Bitartrate	Sodium acid Phosphate	Potassium acid Sulphate	Calcium acid Phosphate	Ammonium Carbonate	Sodium Bicarbonate	Magnesium Carbonate	Farina	Corn Flour	Rice Flour	Starch
1	6						2		1 5			
2	14						16	6	12			
3		2½					2½			4		
4				3			1			1		
5	5	15					20				40	
6			20		20		25					35
7		2					1					1
8			14½				7					3 5
9		60				1	28		16			
10	1						1					
11	35					56						100

641. Adulteration of Flour. Various seeds may become mixed with the wheat, such as the cockel and darnel, or if the wheat is kept in a damp place it moulds and other fungus growths occur. Other grains are often added intentionally to cheapen the cost of production. These are usually rye, corn,

rice, potato starch, and meal from peas and beans. Sometimes alum, borax, chalk or magnesium carbonate is added but when this is done it is usually the fault of the baker instead of the miller.

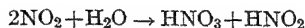
642. Bleaching of Flour. There are several processes for bleaching flour, but they are all substantially the same, since they all make use of nitric oxide to produce the tetroxide which acts upon the fat of the flour. Nitric oxide is the same however made and has the same properties and exerts the same effects upon the flour and the bread.

The Alsop Process, which is probably the best known, uses two electrodes which are made to approach and recede by a mechanical device, while a heavy current is passed through them. This produces a flaming arc which acts upon a current of air that is forced through the tube, causing part of the nitrogen and oxygen to combine and form nitric oxide, N_2O_2 , or NO . This gas reacts with the oxygen of the air to form nitrogen tetroxide, N_2O_4 , or NO_2 , which remains mixed with the air. The modified air is forced into the presence of the flour, which is being continuously passed through a revolving reel or agitator.

The Williams Process passes the current through two electrodes in a cell containing nitric acid, and the fumes are blown into the agitator.

The Naylor and Girard Process obtains the nitric oxide by feeding a No. 4 galvanized wire into nitric acid and the fumes are utilized in the same way as in the other processes, the difference being in the method used to obtain the gas.

643. Action of the Gas on the Flour. Since the flour averages from 10 to 12% water the nitrogen tetroxide reacts with the water and forms equivalent amounts of nitric and nitrous acids



The acids further react with the flour forming nitrates, nitrites, and other nitrite reacting material, known as nitroso and

diazo compounds, poisonous, and dangerous to handle in quantity in the laboratory. Chemical combination probably occurs because experiments show that it is impossible to get back more than 10 to 14% of the amount of gas added to the flour and that this amount becomes less as the time increases.

644. Natural Whitening. Flour left for two or three months naturally becomes whiter and improves in flavor and in the quality of the gluten. When flour is bleached the gluten is said to be less elastic, thus lowering the quality of the flour for bread making.

Although many claim that moderate bleaching produces no harmful effects on flour, all agree that bleaching makes it possible for a miller to sell straights and clears as patent flour. Bran specks are not bleached. Some experimenters say that flour exposed to the air for a few days will take up enough nitrites from the air to react the same as bleached flour.

645. Nitric Acid poured upon bread, will, if sufficiently concentrated, produce a yellow color, the same as when poured upon the skin, known as the xantho-proteic reaction. It is said that the color of the flour is found chiefly in the oil, and that it is a double color—orange and yellow, and that the nitrogen tetroxide reacts first with the orange, and then with the yellow, but that if the reaction continues too long, the yellow color is restored, until it is more than it was at first, and that if the action is still continued the color finally becomes a dark orange.

646. Effect of Nitrites. Nitrogen tetroxide is a dangerous gas to inhale. It produces constipation and interferes with the absorption. The red corpuscles of the blood gradually become rusty, forming methemoglobin, so that they no longer carry oxygen, producing anemia, chlorosis, and death. It affects the walls of the heart and blood vessels, weakens the heart action and lowers the blood pressure. Nitrites are sometimes prescribed medicinally for this purpose. Since the action of nitrites and other drugs is modified by the general health it is not surprising to find that some state that large doses of nitrites taken

internally did not affect the blood so that even with the spectro-scope they were unable to detect methemoglobin in the blood stream. It is also claimed by the advocates of bleaching that the urea will effectively destroy the nitrites as taken in food, so that they declare bleached flour to be perfectly harmless.

647. Good Bread Flour. The exact quality of flour can be determined only by very complicated chemical tests, but the following description of a good bread flour, as given in Farmers' Bulletin No. 389, U. S. Dept. of Agriculture will help. In general housewives prefer flour that is white with a faint yellow tinge. After being pressed in the hand it should fall loosely apart; if it stays in lumps it has too much moisture in it. When rubbed between the fingers it should not feel too smooth and powdery, but its individual particles should be vaguely distinguishable. When put between the teeth it should "crunch" a little. Its taste should be sweet and nutty, without a suspicion of acidity.

648. Losses in Bread Making. There is always more or less loss of material in bread making. With care this may be as low as 1.5% but may be as high as 8 to 10% if handled carelessly in mixing and molding. Moreover, some of the carbohydrates are used by the yeast plants, and the alcohol and some of the fats are vaporized in the process of baking.

649. Imperfections in Bread. *Heavy Bread.* The gluten is too weak or there is too much water in proportion to the flour; too little or too poor yeast, insufficient kneading, rising or baking.

The Crumb Breaks. The flour was dry and harsh, not sufficiently-fermented, or the dough was overworked.

Large Irregular Holes. The bread was over-kneaded or over-raised, or if near the crust the oven was too hot.

Sticky or Slimy Bread. If the bread in three or four days changes to a light brown color and takes on a peculiar taste and odor it is due to the common potato bacillus, entering when the bread is made, and surviving the heat of baking.

Mould. A minute plant, similar to yeast, falls from the air upon the bread, and grows in damp weather.

Sour Bread. This is due to lactic or butyric fermentation, caused by lack of cleanliness or to too many bacteria in yeast which had a chance to grow by letting the bread stand too long after the yeast ceased to work.

650. Other Flours. Rye has less gluten than wheat, while barley, oats and corn have none. Whole wheat and graham flours have more mineral matter, but probably it is not of the same value as the mineral matter of the inner part of the wheat. Although experiments show that the protein of these flours is not more digestible, as often claimed, the use of these flours at least gives a pleasing variety to the diet.

651. Value of Spices in the Diet. While the nutritive value of spices is very slight they stimulate the appetite and increase the flow of the digestive fluids, thereby stimulating the digestive organs, so that the food is more thoroughly digested. It is well known that good food, well cooked, properly seasoned and attractively served in pleasant surroundings tends to arouse the appetite, stimulates the flow of the digestive juices and increases their strength.

652. Common Spices and Condiments. The common spices and condiments are usually of vegetable origin, and are derived from the buds, flowers, fruits, seeds, bark or roots of the plants used. The flavor they impart is due largely to the presence of volatile oils, and while spices are usually not pleasant to eat separately, they are valuable additions to the diet when added in small quantities to food, one or more being used according to individual taste.

653. Allspice, known as Pimenta, and Jamaica pepper, is obtained from the dried nearly ripe fruit of the *Pimenta officinalis*, found in the East Indies, West Indies, Central and South America. It contains volatile oil, resin, tannin, fixed oil, sugar and gum. To be considered pure, allspice must contain not less than 8% of quercitannic acid; not more than 6% of total ash,

not more than 0.5% of ash insoluble in hydrochloric acid, and not more than 25% of crude fiber.

654. Anise, or aniseed, is the fruit of the *Pimpinella anisum*, found in Western Asia, and Egypt, and cultivated in Southern Europe, India and the United States. It contains volatile oil, resin and fixed oil.

655. Bay leaf is the dried leaf of the *Laurus nobilis*, and is also called sweet bay, bay, noble laurel and bayberry. It is found in the Mediterranean region and is cultivated in Mexico. The leaves are from 2 to 4 inches long, smooth, with an aromatic odor and a pungent taste due to the volatile oil. The fruit contains a fixed oil also.

656. Caraway is the dried fruit of the *Carum Carvi*, found in Europe and Central and Western Asia, and cultivated in England, Russia, United States, etc. Caraway contains volatile and fatty oils, resin, sugar, tannin and mucilage.

657. Cayenne and Red Peppers. Red pepper is the red, dried, ripe fruit of any species of *Capsicum*.

Cayenne pepper, called also African pepper, Chillies and bird pepper, is the dried ripe fruit of the small species of *Capsicum*. The fruit has a hot, pungent taste. It contains fixed oils, capsaicin, $C_9H_{14}O_2$, capsacutin, $C_{39}H_{54}N_3O_7$, capscin, capscicol, capscine, oleic, stearic and palmitic acids and coloring matter. To be pure there should be not less than 15% of non-volatile ether extract; not more than 6.5% of total ash; not more than 0.5% of ash insoluble in hydrochloric acid; not more than 1.5% of starch; and not more than 28% of crude fiber.

Paprika is the dried ripe fruit of the large species of *Capsicum*, excluding seeds and stems.

658. Celery, or apium, is the dried fruit of the *Apium graveolens*. The seeds are about 1/25 inch long, ovate, flattened, brown and smooth, containing volatile oil and fixed oil.

659. Cinnamon and Cassia. Cinnamon is the dried bark of any species of the genus *Cinnamomum* from which the outer layers may or may not have been removed. True cinnamon is

the dried inner bark of *Cinnamomum zeylanicum*, while cassia is the dried bark of other species. Cassia buds are the dried immature fruit, and ground cinnamon or ground cassia, is a powder consisting of cinnamon, cassia, or cassia buds, or a mixture of these spices, and contains not more than 6% of total ash and not more than 2% of sand. Cinnamon bark is obtained in the form of quills of varying length, 1/25 inch or more in thickness, nearly deprived of its corky layer. The color is yellowish brown, and when the quill is broken the fracture is nearly smooth. Cinnamon has a fragrant odor and a sweet aromatic taste. The constituents of cinnamon are ethereal oil, cinnamic aldehyde, tannin, mucilage and sugar. Ceylon cinnamon has long closely rolled quills of eight or more layers, of the thickness of paper, while saigon, found in Anam, and cultivated in Java, Sumatra, South America, etc. has quills about 6 inches long, 2/5 to 3/5 inch in diameter with the bark 1/12 to 1/8 inch thick. The taste is somewhat more astringent.

660. Cloves are the dried flower buds of the *Caryophyllus aromaticus*, which contain not more than 5% of clove stems; not less than 10% of volatile ether extract; nor less than 12% of quercitannic acid; not more than 8% of total ash; not more than 0.5% of ash insoluble in hydrochloric acid, and not more than 10% of crude fiber. Cloves are found in Molucca Islands, Zanzibar, Sumatra, South America, West Indies, etc. Cloves contain ethereal oil, eugenol, $C_9H_8.OCH_3.OH$, caryophyllin $C_{20}H_{32}O_2$, tannin, gum and a tasteless resin. Cloves are sometimes adulterated with allspice and with exhausted cloves, after the oil has been extracted.

661. Ginger is the washed and dried, or the decorticated and dried rhizome of *Zinziber zingiber*, and contains not less than 42% of starch; not more than 8% of crude fiber; not more than 6% of total ash; not more than 1% of lime; and not more than 3% of ash insoluble in hydrochloric acid. Ginger contains a volatile oil, an acrid resin and gingerol. Limed ginger, or bleached ginger, is whole ginger coated with carbonate of lime

and contains not more than 10% of ash, not more than 4% of carbonate of lime, and conforms in other respects to the standard for ginger.

662. Mace is the dried arillus of *Myristica fragrans* Houttuyn, and contains not less than 20 nor more than 30% of non-volatile ether extract; not more than 3% of total ash; not more than 0.5% of ash insoluble in hydrochloric acid, and not more than 10% of crude fiber. Mace has a fragrant odor, and contains volatile oil, fixed oil, resin, sugar, mucilage and proteins.

663. Mustard Seed is the seed of *Sinapis alba* (white mustard) *Brassica nigra* Koch (black mustard) or *Brassica juncea* Cosson (black or brown mustard). White mustard contains sinapine, sinalbin, myrosin, erucin, erucic acid, fixed oil, mucilage, behenic acid and sinapolic acid. Black mustard contains sinigrin, $\text{KC}_{10}\text{H}_{18}\text{NS}_2\text{O}_{10}$, myrosin, sinapine, fixed oil, erucic (brassic) acid, behenic acid, sinapolic acid, myronic acid or its potassium salt, mucilage and proteins.

Ground mustard is a powder made from mustard seed, with or without the removal of the hulls and a portion of the fixed oil, and contains not more than 2.5% of starch and not more than 8% of total ash.

Prepared mustard, German mustard, French Mustard, or mustard paste, is a paste composed of a mixture of ground mustard seed or mustard flour, with salt, spices and vinegar, and, calculated free from water, fat and salt, contains not more than 24% of carbohydrates, calculated as starch, determined according to official methods; not more than 12% of crude fiber nor less than 35% of protein, derived solely from the materials named.

664. Nutmeg is the dried seed of the *Myristica fragrans* Houttuyn, deprived of its testa, with or without a thin coating of lime, and contains not less than 25% of nonvolatile ether extract, not more than 5% of total ash, not more than 0.5% of ash insoluble in hydrochloric acid and not more than 10% of crude fiber. The chief constituents are volatile and fixed oils.

665. Pepper. Black pepper is the dried unripe fruit of the *Piper nigrum* found in India, Malabar coast, Philippines, Sumatra, Java, Ceylon, Borneo, etc. It contains volatile oil, piperine, $C_{17}H_{19}NO_3$, piperidine, $C_5H_{11}N$, chavicine, fat, proteins and resin. Black pepper should contain not less than 6% of nonvolatile ether extract, not less than 25% of starch, not more than 7% of total ash, not more than 2% of ash insoluble in hydrochloric acid, and not more than 15% of crude fiber. One hundred parts of the nonvolatile ether extract contain not less than 3.25 parts of nitrogen. Ground black pepper is the product made by grinding the entire berry and contains the several parts of the berry in their normal proportions. Black pepper is adulterated, the chief adulterants being sand, ash, wheat, capsicum, fruit shells, corn products, leguminous starch, pepper shells and dirt, which are mixed with the genuine pepper.

666. White Pepper is the dried mature fruit of the *Piper nigrum*, from which the outer coating or the outer and inner coatings have been removed, and contains not less than 6% of nonvolatile ether extract, not less than 50% of starch, not more than 4% of total ash, not more than 0.5% of ash insoluble in hydrochloric acid, and not more than 5% of crude fiber.

667. Other Spices, used to a more limited extent are coriander, cumin seed, dill seed, fennel, horse-radish, saffron, sage, savory and thyme, but they will not be described.

668. Flavoring Extracts may be made from spice oils or other vegetable oils, and are used in cakes, candies, and other foods that otherwise would lack a pleasing flavor. The most commonly used flavors are vanilla and lemon, but anise, cinnamon, clove, almond, rose, orange, sassafras and tonka are also used.

669. Vanilla Extract is made from the vanilla bean, the fruit of an orchid, a parasitic climbing plant, found in most tropical countries but the best beans come from Mexico. The pods, gathered from May to July, are odorless when picked, the odor developing during a process of sweating—fermentation—after

which they are dried carefully in the sun for about a month or in air dried over calcium chloride. The extract is made by cutting the beans into small pieces, soaking them in alcohol and adding sugar and water. The flavor of vanilla is due to vanillin, a white crystalline substance now made synthetically. From 4 to 11% of resin is also present, while the vanillin varies from 1.7 to 2.75%. Vanilla extract may or may not contain sugar or glycerine, and contains in 100 cubic centimeters the soluble matters from not less than 10 grams of the vanilla bean. From 0.1 to 0.2% of vanillin should be present, from 2 to 4% of resins while if sugar is used it is about 20% and the percentage of the alcohol is 40.

Tonka Beans are found in Guiana, Angostura, etc. The taste is aromatic and somewhat bitter, with a balsamic vanilla-like odor, but this is due to coumarin, instead of vanillin, and is not as pleasant or delicate as the true vanilla. However it is often substituted for vanilla either in whole or in part since it is considerably cheaper. The label must read Tonka Extract or Tonka and Vanilla Extract since it is illegal to sell the tonka as vanilla.

Artificial Vanilla is also made from vanillin, made synthetically, by dissolving the substance in alcohol and sugar, and adding caramel to color the solution the same as vanilla. Vanillin and coumarin are sometimes mixed for the same purpose.

670. Lemon Extract is made by soaking pieces of lemon peel in alcohol, or by dissolving lemon oil in alcohol. The extract made from the peel is yellow, but that from the oil is colorless, so that it is often colored by adding lemon peel extract, or by adding coal-tar or other dyes. Legal lemon extract must contain not less than 5% of oil of lemon by volume. Sometimes it contains more. Lemon oil, made from lemon peel by pressing or by soaking in alcohol contains not less than 4% by weight of citral. This is an aldehyde having the formula $C_{10}H_{16}O$, the same as for camphor. It is a golden yellow liquid having a strong lemon odor, and is often added to oil of lemon used in extracts

to fortify the oil. In order to hold 5% of oil of lemon in solution there must be 80% alcohol. A 45% alcohol will not dissolve any oil but will retain a fairly strong lemon-like odor, so that fraudulent extracts may be obtained that contain little or no oil, but still smell about the same as lemon. Methyl alcohol is sometimes used in place of the more expensive ethyl alcohol, but this is illegal.

671. Names for Artificial and Substitute Flavors. It is the purpose of the Government to have all artificial and substitute flavors properly labeled. If the flavoring substance is not a genuine extract it must be labeled to show that it is not the true extract. As illustrations where vanillin or cumarin is used in the preparation of vanilla extract the labels should read "vanilla and vanillin flavor," "vanillin and cumarin flavor," "imitation vanilla flavor" or "vanilla substitute," using the word *imitation* as preferable to *artificial*. Any artificial or imitation coloring must also be stated.

672. Imitation or Artificial Flavors. A great many of these flavors are manufactured, particularly for use in soda water. The fundamental basis for these flavors is the series of esters, often called compound ethers, to which are added, certain organic acids, as found in fruits, chloroform, aldehyde, glycerin and occasionally a small amount of fruit oils. The substances are added to dilute alcohol one at a time, shaken thoroughly, and allowed to stand until the flavor is developed. Aniline dyes are sometimes used to color them, caramel being added in some. Boric, salicylic and benzoic acids are used as preservatives. The table in §618 shows the composition of a number of the common imitation flavors.

673. Other Extracts Used as Flavors. Most of the other extracts used as flavors are made in the same manner as lemon. The essential oil is added to dilute alcohol or some substitute, shaken and allowed to stand until needed. The following percentage of oil by volume must be found in extracts in order to be exempt from the charge of fraud. Nutmeg, 2%; orange, 5%;

peppermint, 3%; rose, 0.4% otto of roses; savory, 0.35%; spearmint, 3%; star anise, 3%; basil, 0.1%; marjoram, 1%; thyme, 0.2%; wintergreen, 3%. Ginger extract must contain in each 100 cubic centimeters the alcohol soluble matter from 20 grams of ginger. Almond, 1%; anise, 3%; celery seed, 0.3%; cassia, 2%; cinnamon, 2%; clove, 2%. More than these amounts may be in the extract but no less without being branded as adulterated, and the manufacturer is liable to prosecution.

674. In the Non-alcoholic Extracts, olive, cottonseed or neutral lard oil is used in place of the alcohol. The essential oil, is heated with about 10 times its weight of olive or other oil substitute on a water bath for 30 minutes to a temperature of 70° to 80°. It is then strained through felt. When vanillin and cumarin are used to make imitation vanilla from 2 to 2.5% is soluble. Since the oils used act also as shortening, somewhat less butter or other shortening substance may be used.

675. Coffee is prepared from the dried, roasted and ground seed of *Coffea arabica*, an evergreen shrub indigenous to North-east Africa and Arabia. The young plants are reared in nurseries and are transplanted after six months to two years. Fruit is produced the fourth year and bearing continues for several years. The tree blossoms and bears fruit practically the entire year. It requires about four months for the fruit to ripen. (See Fig. 155.)



FIG. 155. Coffee, Cross Section and Longitudinal Section.

The color of unroasted coffee varies from pale yellow through green to slaty gray. The seeds vary considerably in size, from 187 of Java to 313 of West African being

required to fill 50 cubic centimeters.

676. Roasting develops aroma and destroys toughness, but unless carefully watched is apt to be either too little, making the coffee hard to grind, or too much, bringing out a disagreeable flavor. During roasting from 15 to 18% by weight is lost of

which half is water and the rest volatile products derived from fat and from sugar which is converted into caramel. An empyreumatic oily substance known as *cafféol* is developed which gives much of the aroma. The temperature for roasting is a little above 200° . After roasting the coffee should be cooled rapidly on sieves, through which an air current is passing. Coffee should not be ground until needed since the essential oil escapes rapidly when the seeds are broken.

677. The Distillation of the Volatile Substances produced during roasting gives a watery liquid and a solid portion. The former has been found to contain caffeine, *cafféol*, acetic acid, quinol, methylamine and acetone; the solid portion is chiefly palmitic acid. Pyrrol escapes during roasting.

678. Various Analyses of Coffee give the chemical composition as gummy matter, 20.6 to 27.4%; caffeine, 0.64 to 2.21, with an average of 1.16; fat, 14.76 to 21.79; tannic and *caffetannic* acids, 19.5 to 23.1; cellulose, 29.9 to 36.4; ash, 3.83 to 4.87, averaging 4.41; phosphoric acid, 0.28 to 0.72, averaging 0.42; and in some coffees potash, 1.87 to 2.13. Other constituents are *cafféarin*, protein, sugar and mineral matter in small amounts.

679. Caffeine, $C_5H(CH_3)_3N_4O_2$, or trimethylxanthine is identical with theine, the alkaloid of tea, and is closely related to theobromine, or dimethylxanthine, the principal alkaloid of cocoa. It is thought that caffeine in coffee occurs as potassium *cafféinechlorogenate*, $C_{32}H_{36}O_{12}K_2(C_8H_{10}N_4O_2)_2 \cdot 2H_2O$. When pure, caffeine occurs as white silky needles, slightly bitter and odorless, and almost insoluble in ether, sparingly soluble in water and alcohol, but more soluble in hot water, and more soluble in chloroform, by means of which it may be extracted from coffee. It is also found in Kola nut, mate or Paraguay tea, and to a small extent in cocoa, and gives to these substances their exhilarating qualities. Small doses of caffeine stimulate the nervous system, the respiration, the vaso-motor centers and the reflexes. It stimulates the heart and relaxes the blood

vessels. The flow of urine is increased; muscular contraction is facilitated and fatigue lessened. Excessive doses produce insomnia, nervousness, headache, palpitation and nausea or vomiting, and lessen the capacity for mental or muscular work. It is sometimes used as a nerve stimulant in cases of nerve exhaustion or collapse, and in cases of narcotic poisoning. The dose is from 0.1 to 5 grains, i.e. 0.06 to 0.3 gram, and when taken in the form of coffee, made by using one tablespoonful to the cup, each cup will contain from $1\frac{1}{2}$ to 3 grains. Hence, while a single cup of coffee may do no particular harm, averaging about half of a maximum dose, the drinking of two or three cups of coffee at a meal is not to be recommended.

680. The Mineral Matter of coffee, as shown in the ash, is composed chiefly of potash, K_2O , 60 to 63%; magnesia, MgO , about 11; lime, CaO , 5 to 7; phosphoric acid, 11.5 to 14; with smaller amounts of silica, SiO_2 ; ferric oxide, Fe_2O_3 ; soda, Na_2O , sulphuric acid, and chlorine.

681. Coffee is Adulterated (1) by coloring the damaged beans when raw by chrome yellow, yellow ochre, indigo, Prussian blue, or when roasted, by burnt umber, iron oxide, Venetian red, ferruginous earth etc. (2) by glazing with egg albumen and glucose or gum, or first by steaming and coating with glycerine, palm oil or vaseline to prevent the escape of moisture, which may add about 12% to the weight. (3) by the addition of chicory, acorns, beet refuse, biscuits, bran, various cereals, burnt sugar, dandelion roots, parsnips, peas, beans, turnips, coffee husks, cassia seeds, date stones, grape seeds, sawdust, vegetable ivory, dust, etc. These may be detected either by the microscope, or if boiled in water by the starch test, coffee being practically free from starch. The presence of adulterants may also be detected by a difference in the specific gravity of the solutions made from one part of the substance by weight to 10 of water. The mixture is boiled for one-half minute, filtered and cooled. Coffee thus prepared has a specific gravity of 1.0084 to 1.0095. Acorns and peas would give a specific gravity test of

1.0073 while most of the other adulterants yield decoctions whose specific gravities vary from 1.0143 to 1.0163, very much higher than coffee. Since chicory is the chief adulterant used and the specific gravity of a chicory decoction varies from 1.0226 to 1.0232 it may easily be detected. If a mixture of chicory and coffee is placed on the surface of water in a glass the chicory produces streaks colored brownish yellow and sinks, while coffee produces no coloration and nearly all of it floats.

682. Tea. Black and green teas are not obtained from different plants, but may be taken from the same plant, the difference in the final product depending upon the mode of preparation, and partly upon the time of gathering the leaves and the method of rolling them. Fig. 156 illustrates a tea leaf.

Green Teas are divided into several classes, of which the following varieties are well known: *Hyson*, *Skin Hyson*, and *Gunpowder*, while among the well known *Black Teas* are *Pekoe*, *Souchong*, *Congou*, *Bohea*, *Moning* and *Oolong*.

Hyson is made from the leaf buds and first leaves, picked in April, and when rolled are given a spiral twist. *Skin Hyson* is made from inferior leaves and in rolling them tea refuse is often enclosed. *Gunpowder* is a carefully selected *Hyson*, and is often flavored with the sweet scented olive.

Pekoe is made from the youngest leaves and is picked in April. *Souchong* is the strongest of the black teas and is made from the largest of the young leaves. *Congou* is made from the younger leaves of the third crop, the leaves being older and larger than those used for *Souchong*. *Bohea* is made from the older leaves of the third crop. *Moning* and *Oolong* are black teas with a green flavor and are used largely in blends.

683. In Preparing Green Teas the object is to keep the color and to prevent fermentation, so that the leaves are pre-

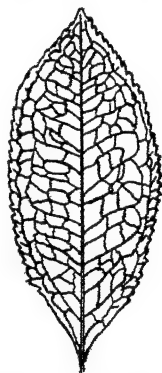


FIG. 156 A Tea Leaf

pared as soon after picking as possible and the process is finished rapidly. For *Black Teas* the leaves are dried slowly and fermentation is a part of the process.

In the Chinese Method for Green Teas the leaves are first steamed, then dried in the shade. They are then roasted over a wood fire in an iron pan for four or five minutes. After rolling the leaves they are roasted again, this time over a charcoal fire for an hour to an hour and a half, in order to fix the color, which gradually becomes brighter. The leaves are then sifted and finally given a third roasting for five minutes. The method used in Japan is essentially the same with modifications in minor details.

In India the Green Teas are first dried, then roasted with stirring at 160° for seven minutes. They are then rolled four times and are dried in the sun between consecutive rollings. A second roasting at the same temperature follows, after which the leaves are beaten in bags. They are then set aside until the next day when a third roasting is given, the temperature gradually falling from 160° to 120° , after which the leaves are sifted and sorted. Ceylon methods are essentially the same as those of India.

684. In Preparing Black Tea the Chinese first wither the leaves by out of door exposure for several hours. They are tossed, and finally covered with a cloth in the shade or in a cool building and allowed to ferment until soft and fragrant. The first roasting and rolling are the same as for the green teas. The leaves are then exposed out of doors for three hours, and are then roasted and rolled in the same manner a second time. They are then dried, rolled and sifted and finally dried over a slow fire for two hours.

In India the Black Tea is prepared by first withering the leaves, which are then rolled vigorously until the juice begins to come out. The leaves are then rolled into balls with the juice and are fermented until exactly the right condition is reached, after which the balls are broken up and spread out in the sun.

The leaves are then dried over a charcoal fire or with hot air and sorted.

685. Composition of Tea. The analyses of various kinds of tea show that the water extract varies from 38.43 to 49.75%, the caffeine from 2.34 to 4.96; the tannin from 7.272 to 14.98; the ash soluble in water from 2.76 to 3.70; the ash insoluble in water, less the silica, 1.77 to 2.98; the silica, chiefly sand, 0.03 to 2.74; total mineral matter 5.14 to 8.87; total moisture, 5.60 to 9.70.

686. The Amount of Tannin is somewhat less in black tea than it is in the green, because of the change of part of the tannin to insoluble substances during fermentation. In some of the very astringent teas the amount of tannin is considerably more than the average amounts just stated, sometimes going as high as 42.3%.

687. The Mineral Matter as found in the ash when tea is burned varies from about 5 to 9% but more frequently averages from 5 to 7%. It usually averages potash, 38.22%; phosphoric acid, 14.55; carbon dioxide 24.30; magnesium oxide, 6.47; iron oxide, 4.38, silica, 4.35; lime 4.24; manganous oxide, 1.03; chlorine, 0.81; soda, 0.65; sulphuric acid, trace.

688. The Essential Oil of tea occurs in very small amounts. When 440 pounds of fresh leaves were distilled with water, one investigator obtained only traces of the oil; but when 100 pounds of the rolled and fermented leaves were used, 3 cubic centimeters of the oil were obtained. The oil is yellowish in color, has a strong odor of tea, and is classed as an unsaturated alcohol having the formula $C_6H_{11}OH$.

689. Nitrogen is present in tea leaves to the extent of 5.1 to 6.62%, considerably higher than in most leaves. It is found in the caffeine and in albuminous bodies.

A strong decoction of tea frequently becomes turbid on standing and cooling and may be covered with a thin membrane. This is caused by the separation of caffeine tannate. This will

become darker on standing, due probably to an increase of the amount of tannin and alteration by oxidation.

690. Tea Is Adulterated by the addition of other leaves such as the ash, beech, birch, chestnut, currant, plum, willow, etc. or by adding exhausted tea leaves. Graphite is sometimes added to black tea, while indigo, Prussian blue, turmeric, etc. may be added to the green. Iron sulphate is sometimes added to increase the astringency, and sand to increase the weight.

691. Cocoa, described with chocolate as a food, (see §579) is used as a beverage. The composition of cocoa shows fat, alkaloids, albuminoids, starch, tannin, coloring matter and mineral matter.

Cocoa fat, known as cocoa butter or oleum theobromae constitutes 45 to 55% of the cocoa. It melts at 28° to 33° and becomes solid at 21° to 23°. Its specific gravity varies from 0.95 to 0.97 at 15°. It is soluble in ether, chloroform, turpentine and boiling alcohol. Chemically it is a mixture of the glycerides of stearic, palmitic, oleic and arachidic acids. It is adulterated with cocoanut oil, cotton seed oil, sesame oil, stearin, paraffin, tallow, etc.

692. The Alkaloids of cocoa are theobromine, $C_5H_2(CH_3)_2N_4O_2$, chemically known as dimethylxanthine and caffeine. Theobromine occurs to the extent of 1.5%, and may be obtained as white microscopic needles, bitter to the taste. Caffeine is found in much smaller quantities, 0.1 to 0.3%.

The Albuminoids are divided into several classes (1) non-proteins including theobromine, ammonia, amino-compounds; (2) digestible albumen, soluble when treated with gastric juice and alkaline pancreatic extract; (3) insoluble and indigestible nitrogenous substances. The total albuminoids constitute about 17 to 18% of the entire cocoa, from 60 to 80% of the total albuminoids being digestible.

693. Starch occurs in cocoa to the extent of 4 to 5%.

Tannin occurs in the raw beans, which are nearly white, but

is not found in the roasted beans since it is oxidized to *cocoa red* the coloring matter of the finished product.

The Mineral Matter varies from 2.5 to 4.5%, averaging 3.6%, in the raw and 3.9% in the roasted beans.

Cocoa ranks higher than either tea or coffee as a nutritious beverage but probably not as high as usually believed. On account of the alkaloids and the tannin it should be regarded as a stimulating beverage rather than as a true food. As a beverage it is usually mixed with milk and sugar and is stirred while being brought to a boil.

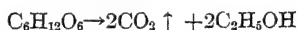
694. Soda Water or carbonated water is made by forcing carbon dioxide into a tank of water, until the pressure is from 4 to 10 atmospheres. When the pressure is removed by opening the valve, some of the charged water is forced out into the glass and the reduced pressure causes the gas to escape forming bubbles. Soda water usually contains a syrup, either natural or artificial, to give a certain flavor, and may contain ice cream, crushed fruits, nuts, etc. With a pure grade of ice cream and pure fruit flavors there is nothing especially harmful in the beverage. Some of the artificial flavors, however, contain substances which, if taken in quantity for any considerable period may produce harmful effects. The table in §618 shows the composition of the more commonly used artificial flavors.

695. Alcoholic Beverages. A large number of alcoholic beverages are used by many people, as either a stimulant, a drink or a food. Concerning the latter use it may be said that alcohol stands between sugar or starch and carbon dioxide, the final product of the burning of these substances. In composition alcohol is simpler than the fats which are oxidized in the body, so that alcohol ought to be more easily oxidized than fats, and the use of alcohol should effect some saving. Many experiments which have been tried to test this theory have, however, proven the contrary, and have shown that *for people in good health alcohol furnishes an extremely small amount of nourishment*. In cases of illness the body may at times be able

to oxidize small amounts of alcohol, more easily than it can oxidize the ordinary fats so that loss of energy may be stopped by the use of a moderate amount of wine or champagne. This should, however, be administered by a physician, and should not be left to the desires of the patient any more than the use of any other dangerous substance.

Ethyl alcohol, C_2H_5OH , commonly known as grain alcohol, is always obtained from the fermentation of sugar, which may be derived from the starch of corn, rye or barley by conversion with diastase, or from molasses.

The grain is ground, mixed with water, and heated. Malt is added, the mixture is filtered, and then yeast is added. Fermentation of the glucose occurs, producing carbon dioxide and alcohol, according to the equation



The alcohol yield is from 10 to 13%, the rest being water, fusel oil, acids, etc., from which the alcohol is removed by fractional distillation. After two or three distillations a mixture containing 96% by weight or 97.4% by volume of alcohol is obtained.

Absolute alcohol is obtained by removing the water. This is brought about by the action of dehydrated copper sulphate, or barium oxide, the last traces being removed by metallic sodium.

Alcohol boils at 78.3° and has a specific gravity of about 0.794. It burns with a non-luminous flame, depositing no soot, and produces about twice as much heat as gasoline. Taken internally it lowers the temperature of the body from 0.5 to 2 degrees. In small amounts it is oxidized, and seems to act as a food, but in larger amounts it intoxicates and acts as a poison.

For many industrial purposes it is sold as denatured alcohol. Since January 1, 1907, the use of denatured alcohol has been permitted without paying the government tax. The process of denaturing consists in adding certain substances to the ordinary alcohol which will render it absolutely unfit for

drinking purposes. There are about 65 different approved formulas for denaturing, the one used depending upon the future uses of the alcohol being treated. Wood alcohol, CH_3OH , made from the destructive distillation of wood, is often used for this purpose. Pyridine, or bone oil, is also used giving a very offensive odor. Some formulas call for both, either with or without the addition of benzine.

CHAPTER XXVIII

PRESERVATION AND DYEING OF FOODS.

696. Since the law provides that no food or food product shall contain substances which lessen the wholesomeness of the food or which add any deleterious properties thereto, it has been determined that no drug, chemical, or harmful or deleterious dye or preservative may be used.

Substances Permitted as Preservatives. Common salt, sugar, wood smoke, potable distilled liquors, vinegar and spices or condiments may be used for the preservation of food. A recent decision permits the use of sodium benzoate and pending further investigation the use of saltpeter and, to a limited extent, sulphur dioxide is permitted.

Substances Not Permitted. Borax, boric acid, salicylic acid and its salts, benzoic acid and its salts, other than sodium benzoate are considered injurious to health and should not be added to food, if the food can be kept without them.

697. **Preserving Foods Without Violating the Law.** There are a number of methods of preserving foods that are permissible. One of the oldest and best known is by *drying*. This method is easier in a hot dry climate than elsewhere, since there is danger of fermentation and decay in cold, damp climates. Preservatives are sometimes added to dried foods, as sulphur dioxide to dried fruits. Dried and heated air is also used instead of sun drying. In any case sanitary conditions must be observed and the food must not be exposed to flies.

Cold Storage. In cold storage the temperature varies from 10°C to below freezing. Slight changes in composition and flavor are brought about, but the juices remain the same. Meats are frozen solid. Fish are frozen solid, then dipped into water and frozen again so that they are encased in ice. When

removed from storage meats and fish should be thawed slowly so as to keep the flesh firm. Preserved in this manner meats are kept for several months and some are said to keep for years. Fruits and vegetables are not frozen, but the temperature is kept near 0°C.

High Temperatures. Temperatures varying from 65° to 120°C are also used. Heat kills bacteria and this method is valuable for milk, fruits, vegetables, meats, etc. The jars in which the food is kept should preferably be either glass or porcelain, since vegetable and fruit acids dissolve lead, which is often found as an adulterant of tin. Only the best grade of pure tin should be used in cans for fruits and vegetables and no solder should come in contact with the contents of the can.

Smoking as a Preservative. Although wood smoke contains creosote and other substances that would be harmful if taken in large amounts, the quantity consumed in smoked foods is very small so that no ill effects are observable. The same effect can be obtained more rapidly if the food is dipped into a solution of pyroligneous acid, but the flavor is not the same.

Salt is not a very effective preservative. Salt is used also as a condiment and has a food value as well. It is considered necessary for most individuals as well as for cattle to consume a certain amount of salt.

Spices. Although spices have preservative powers they cannot be used in large enough quantities to preserve foods. Their use is chiefly to produce an added taste. Spices stimulate the flow of the digestive fluids and thus serve as an aid to digestion. See also Chapter 27.

Sugar, in dilute solution permits the rapid growth of bacteria, but if the solution is very concentrated the growth is almost entirely prevented. For that reason jams and jellies usually keep well, and candy will keep almost indefinitely.

698. Effect of Chemical Preservatives on Food. Chemical preservatives do not prevent the growth of bacteria, but retard only certain kinds, namely those producing a bad odor and taste,

while the others are permitted to grow rapidly, so that samples of spoiled preserved foods may contain several times as many bacteria as spoiled unpreserved foods. The consuming of bacteria is considered harmful and tends to increase the death rate. The use of chemical preservatives permits the use of food that would otherwise be condemned as unfit for food. The use of preservatives does not tend to promote cleanliness and sanitary methods of handling and storing foods. Examples of the pernicious use of chemical preservatives may be seen in the handling of tomato pulp, ketchup and liquid eggs.

699. Use of Sulphur Dioxide. Sulphur dioxide may be used as a preservative if the total amount in the finished product is not more than 350 milligrams per liter in wines, or 350 milligrams per kilogram of other food products, of which not over 70 may be in a free state. Dried and evaporated fruits as analyzed sometimes show from 1400 to 3000 milligrams per kilogram. The bright red color of Hamburg steak and some sausage is due to sulphur dioxide. Hamburg steak is usually made from the trimmings and pieces of stale meat that could not otherwise be sold.

700. Use of Benzoate of Soda, $C_6H_5CO_2Na$. The use of sodium benzoate is permitted provided that each container or package of such food is plainly labeled to show the presence and amount of benzoate of soda. This decision was reached after a series of experiments using as a small dose 0.3 gram per day and as a large dose as high as 4 grams per day. Since 0.1% is sufficient as a preservative, it would require 300 grams of the preserved food to yield a small dose of sodium benzoate and 4000 grams or nearly nine pounds to yield the maximum. The finding of the investigators was that the use of sodium benzoate in small amounts was not injurious, and that the use of it in large quantities, up to 4 grams per day, was not found to exert any deleterious effect upon the general health, nor to act as a poison in the general acceptance of the term. In some tests there were slight modifications of certain physiological processes, the exact

significance of the modifications not being known. In general, benzoic acid and its salts act the same as salicylic acid and its salts, but in a much milder degree. See Food Inspection Decision 104.

701. Action of Prohibited Preservatives. Borax. The continuous taking of even small doses produces a deleterious effect. Moderate to large doses cause nephritis. Very large doses also cause gastro-enteritis, skin eruptions, visual disturbances, fall of temperature, collapse and a widespread fatty degeneration.

702. Salicylic Acid acts as an irritant to the mucous membranes, and is somewhat corrosive.

Sodium salicylate is the usual form in which salicylic acid is used. Its effects are about the same as those of the acid. On an empty stomach it may cause pain, and in large doses may produce vomiting. Ringing in the ears, sweating, nausea and an increase in the amount of the urine are also produced. Very large doses may produce depression of the central nervous system, rarely convulsions, a slowing and depression of the respiration, and collapse from depression of the circulation. It relieves the local symptoms and fever of rheumatism while the medication is continued, and is beneficial in threatened appendicitis.

703. Formaldehyde. A solution containing 1 part of formaldehyde in 5000 will prevent the growth of many organisms, and a solution of 1 part in 20,000 to 30,000 prevents the multiplication of bacteria. It hardens living tissues and living skin, is very irritating and produces disturbances of the digestion.

704. The Use of Dyes. The use of any dye, harmless or otherwise, to color or stain a food in a manner whereby damage or inferiority is concealed is specifically prohibited by law. Certified coal-tar dyes may be used if they do not conceal damage or inferiority, but a certificate showing that the dye in question has been tested by competent experts and found

to be free from harmful constituents must be filed with the Secretary of Agriculture and be approved by him. Uncertified coal-tar dyes are likely to contain arsenic and other harmful material. Each of these colors shall be free from any coloring matter other than the one specified and shall not contain any contamination due to imperfect or incomplete manufacture. A list of permissible dyes may be obtained from Washington.

Use of Copper Salts. The use of copper salts to produce a green color in foods is prohibited by law. Foods thus greened are denied entry into the United States, and such foods manufactured, offered for sale or shipped in interstate commerce in the United States are considered adulterated.

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CHAPTER XXIX

CHEMISTRY OF THE FERTILIZATION OF SOILS

705. Meaning of the Terms. The subject of fertilization of soils deals with (1) the foods required for the growth of plants; (2) the analysis of soils, to learn whether these foods are present and in what proportion; (3) the analysis of commercial fertilizers to learn whether they contain the necessary foods in the proper proportion; and (4) the correct methods of applying the fertilizer to the soil in order to secure the best plant growth. In other words the question is how to feed the plants in order that they may yield the best returns for the money and labor expended upon them.

706. When Fertilization Is Necessary. If all crops raised were fed to cattle and the manure saved and returned to the soil, the fertility would be practically unchanged; or if crops poor in fertilizing value were exchanged for feed of high fertilizing value it might even be increased. Where such crops as grain, which contain more fertilizing constituents than the waste that can be returned to the soil, or where the same crop is raised every year, the fertility decreases, producing a decrease in the crops, without producing any decrease in the expense of seeding or in the labor involved to raise them.

The chief elements drawn from the soil are potassium, calcium, sulphur, phosphorus and nitrogen; other elements such as silicon, magnesium, iron, sodium and chlorine are taken up to a less degree. The natural weathering of minerals in the ground, together with decaying vegetation, usually provide the elements necessary to plant life, but by frequent repetition of the same crops on the same land, the supply of potassium, phosphorus and nitrogen may be insufficient, and become exhausted.

The soil becomes less and less productive, and finally the crops are a failure.

To supply the continued drain on the soil, and keep it in a fertile condition, fertilizers are used; much more now than when the country was new. The natural fertilizers—barnyard manure, urine, and decomposing vegetable mould or muck, such as straw, cornstalks, etc., were formerly used almost exclusively. But as the land became worn out resort had to be made to artificial fertilizers.

Different soils require these elements in different proportions owing to different formation, or to different management and the crops grown. Sandy soil usually lacks all fertilizing elements, while clay soil usually contains mineral elements in abundance. Soils rich in vegetable matter may lack the mineral matter. Limestone soil usually contains phosphoric acid. Fig. 157

PLANT CONSTITUENTS FOUND IN THE SOIL

NECESSARY	{	WATER	
		SULPHUR	
		MAGNESIUM	
		IRON	
		LIME	— SWEETENS
		NITROGEN	— STALK GROWTH
		PHOSPHORIC ACID	(GRAIN MATURITY QUALITY)
	{	POTASH	— STRENGTH
UNNECESSARY	{	SODIUM	
		CHLORINE	
		SILICON	
		MANGANESE	

FIG 157. Plant Constituents.

shows the plant constituents found in the soil. Water must often be applied by irrigation. See Fig. 158.

707. Needs of Plants. Different crops need these elements in different proportion and unless care is taken to apply the right quantity much will be wasted because of excessive amounts used. This will be lost entirely unless careful culti-



FIG 158. An Artesian Well for Irrigation

vation is applied together with the use of absorbents, followed by crops that can take up the excess readily. For example, legumes, as peas, beans, lentils, etc., take nitrogen from the air by means of nitrifying bacteria on their roots, and the application of nitrogen as nitrates is unnecessary; clover and alfalfa do the same, but grasses and grains cannot do this and have to be fed with nitrogen. See Fig. 159.

708. Artificial Fertilizers are those manurial substances, prepared from materials which need some special treatment to render them fit for plant food. The chief requisites of a good fertilizer are: (1) it must contain at least one substance fit for plant food, and this substance must be easily convertible, by rain and moisture, to such a form that the plants can easily assimilate it; (2) it must be dry and finely powdered, so that it will not deteriorate and it may be evenly distributed over the

surface of the ground; (3) it must contain nothing injurious to plant life; (4) it must be cheap.

There are three elements from which fertilizers are named. These elements are potassium, phosphorus and nitrogen; and we have potassium, phosphatic and nitrogenous fertilizers. Although some fertilizers contain only one or two of these elements, and are sold for certain crops, or for use on particular kinds of soil, a complete fertilizer contains all three of the elements mentioned. The source and composition of the different kinds will be briefly discussed.

709. Potassium Fertilizers. The four forms of potassium fertilizers most commonly used are potassium chloride, potassium sulphate, kainite and potassium carbonate (wood ashes). The formula for kainite is given in various ways, such as $\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, with 15.87% K, or 19.12% K_2O ; $\text{MgSO}_4 \cdot \text{KCl} \cdot 3\text{H}_2\text{O}$, with 15.65% K, or 18.85% K_2O ; or $\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot \text{MgCl}_2 \cdot \text{H}_2\text{O}$, with 18.93% K, or 22.8% K_2O .

Potash is a name given to various potassium compounds, and applies chiefly to the sulphate or the chloride, although other compounds are fully as soluble and are probably as easily decomposed for use by the plant. The acid radical combined with the potassium has a bearing, however, upon certain forms of plant life, the chloride acting unfavorably upon tobacco and potatoes while the sulphate and other forms give favorable returns. The chloride is somewhat richer than the sulphate in potassium, having a little more than 52% when pure, while the sulphate under the same conditions has a little over 44%. Actual analysis shows that the salts as used are somewhat lower in the percentage of potassium than the figures just given, owing to the presence of impurities, such as sodium chloride. The double sulphate of potassium and magnesium is sometimes used, and contains 26.5% of potassium, though much of it is of lower grade. Kainite and sylvanite are crude mine products each containing about 12.5% of potassium. Kainite is mined at Stassfurt, Germany, and is used in the manufacture of most

fertilizers. The supply of kainite in these mines is said to be inexhaustible. The supply of potassium in other parts of the world up to the present time has been quite limited, and to this fact Germany's practical monopoly of the potassium fertilizer industry is due. Potassium chloride is a manufactured product and as sold contains about 45 to 50% of potassium. Potassium sulphate is made from kainite, and contains about 45% of potassium. Wood ashes contain from 2 to 8% of potash which is very soluble and leaches away easily. Wood ashes make a valuable fertilizer and should be carefully saved.

The cutting off of the supply of potash was a serious handicap in the growing of crops in the United States and other Allied countries while its increased consumption in Germany and Austria aided those countries in the production of food.

710. The Potash Supply of the World. It has been estimated that potassium oxide or potash averages 2.98% of the entire crust of the earth. Although silicate rocks contain potash it is in an insoluble combination and in a form which is not available for industrial use. They are generally decomposed on exposure to the weather. The potash thus rendered soluble is dissolved by rain or ground water and it finally reaches the ocean or other drainage basins through the streams or is absorbed by clays from the water penetrating them. River waters of North America contain an average of 281 parts per million of dissolved salts averaging 1.77% potassium. They carry annually to the ocean 8,339,800 metric tons of potassium and the river waters of the world carry 57,892,000 metric tons. The annual precipitation of potassium in insoluble form in the ocean is 50,320,000 metric tons leaving an annual net gain of potassium by the ocean of 7,662,000 metric tons. The total potassium content of the ocean is 510,800,300,000,000 metric tons. Ocean water contains about 3.3% salts of which 1.11% is potassium corresponding to 1.38% of K_2O . The largest potassium salt deposits are found in Germany about 2,000,000,000 tons; Alsace 300,000,000 tons; California

20,000,000 tons and the new found deposits in Africa. with smaller deposits in Spain, Galicia, Abyssinia, etc.

In 1918 the potash bearing materials reported in the United States amounted to 207,686 short tons, having an approximate average content of 26.4% K_2O , equivalent to a total content of 54,803 short tons of K_2O . This was 70% more than the amount reported in 1917 and represented about 22% of the normal consumption which is estimated about 250,000 tons annually. The production came from ten different classes of raw materials. Natural brines furnished about 73% of the output; the Nebraska lakes alone contributing about 53%; and Searles Lake, California, gave the second largest quantity from a single source. Kelp yielded about 9% of the total production followed by smaller contributions from molasses, alanite, cement, dust from glass furnaces, slate rocks, water from beet sugar refineries, wood ashes and the water from washing wool. The average cost to the consumer was \$4.11 per unit of potash—that is, 20 pounds of K_2O —while the imports from Germany during the same year amounted to 7,957 tons, costing \$1.12 per unit. The chief imports for use in fertilizers include kainite, manure salts, chloride and sulphate, and before the war these constituted about 94% of the total potash imports but this dropped to 3.3% in 1918. Kainite is the lowest grade material imported. It is a double salt containing potassium chloride and magnesium sulphate with 3 molecules of water of crystallization. Theoretically it contains 18.9% of K_2O . The product shipped is heated with much sodium chloride and is sold under the guarantee that it contains a potash content of 12.4%. In 1913 kainite constituted about 24% of the total potash imports.

711. Manure Salts are essentially mixtures of potassium chloride, sodium chloride and magnesium sulphate and are low grade fertilizers. Several grades are produced which contain from 20 to 30% of potash. Nearly all material of this class, however, comes to the United States as the 20% grade. Before the war manure salts constituted about 18% of the

potash imported. The chloride fertilizer commonly called muriate is a high grade fertilizer containing about 80% potassium chloride and 20% sodium chloride and formerly constituted about 44% of the total potash imported.

Potassium sulphate imported usually contains about 90% potassium sulphate. It is principally used in fertilizers especially for growing tobacco, but is also used in connection with muriate in various chemical industries.

712. The Effect of the World War upon the prices was very marked. Before the war the most efficient German mines could produce muriate containing approximately 50% of K_2O at about \$15.00 a ton and kainite containing a guaranteed minimum of 12% of K_2O at less than \$2.00 a ton at the mines. Shipping and other costs varied from about \$3.00 to \$4.00 a ton. After the embargo of January 30, 1915 placed on the exportation of potash salts from Germany, the prices of these salts rose rapidly. By the end of the year 80% muriate was selling for \$500.00 a ton with only a very limited amount available.

For many years practically all the potash imported into this country came from Germany. During the war imports from various parts of the world represented both accumulated stocks and domestic production. At least 20 different countries sold potash to the United States during the latter part of the war.

713. Potash Is Used as a fertilizer chiefly in growing cotton, potatoes, tobacco, citrous fruit and garden truck. In 1913 more than 90% of the world's production was consumed in this manner. In the form of refined potassium salts potash is also used in the manufacture of soap, glass, matches, explosives, fire works, medicine, for extracting gold from its ores, in dyeing, tanning, electroplating, photography and as chemical reagents. Potassium salts are used to best advantage on light sandy soils, humus soils and soils containing lime. Sandy soils should have lime added to make them retain the potassium mostly

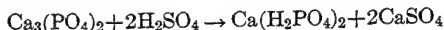
near the surface. Potatoes and beets usually give good returns with potassium, but unless the salt is applied several weeks before the crop is planted the potatoes will be found to be deficient in starch and the beets in sugar. When the chloride is used frequently or in large quantities with lime, calcium chloride, CaCl_2 , is formed, both depleting the lime and acting as a poison to the plants especially in acid soils, and if kainite or other salts rich in chlorine are applied to the soils rich in organic matter, as reclaimed swamps and marshes, the results are not as satisfactory as with the sulphate. If lime is added in this case to counteract the effect of the chlorine, the organic matter is oxidized too rapidly.

714. Potash in the United States. In Searles Lake, California, it is estimated that there are 20,000,000 tons of potash equal to the normal needs for 100 years. In Nebraska there are at least 3,000 deposits covering from 1 to 600 acres each. In one county, in Wyoming, it is estimated that there are at least 200,000,000 tons of leucite rock of 11% pure potash content. The existing plants can produce 75,000 tons annually. In Western Texas beds of potassium bearing rock, containing 15.6% of K_2O , of equal richness of the deposits found in Alsace have been discovered while drilling for oil but it is not yet known how extensive these beds are.

715. Phosphate Fertilizers. The phosphate fertilizers are nearly always applied to the soil in some form of calcium phosphate derived from the phosphates of calcium, iron or aluminum, and occurs in three forms (1) that which is readily soluble in water, and easily used; (2) that which is slightly soluble in water, but still used readily, and known as "reverted" phosphoric acid; (3) that which is sparingly soluble and used but very little.

The average amount of phosphate rock used in the United States per year is about 2,500,000 long tons. The largest deposits are found in Florida, Tennessee, South Carolina and Kentucky with smaller amounts in Idaho, Wyoming and Utah.

It is also found in varying amounts throughout a large part of the earth. These rocks are ground and treated with sulphuric acid, which unites with the calcium and makes the insoluble phosphates soluble, a form in which it is available to plants. Besides the acid phosphate, calcium sulphate is formed thus:



The resulting mixture is a fine powder, which is sold as a fertilizer under the name "acid phosphate" or "superphosphate of lime." It contains about 15 to 20% of soluble phosphorus.

Superphosphates contain reverted phosphates as well as the soluble variety. When made from bone black and bone ash, superphosphates contain about 16% of available phosphoric acid and some nitrogen; when made from mineral phosphates, about 14% of available phosphoric acid, besides 1 to 3% of the reverted and more or less of the insoluble variety.

Double Superphosphates are made by dissolving rock or bone in sulphuric acid containing a large amount of free phosphoric acid, so that the final product may contain as high as 40% of phosphoric acid.

716. Phosphatic Slag is another very fruitful source of phosphates. This is now used to a considerable extent as a fertilizer, especially in Europe and to some extent recently in the United States. In the process of making Bessemer steel, pig iron from ores containing phosphorus, is treated with lime, while a blast of air is forced into the liquid mass. At the high temperature of the melted iron, the phosphorus is oxidized to phosphorus pentoxide, which combines with the lime. The silica, alumina, lime and magnesia unite to form a slag, into which the calcium phosphate produced also goes. By proper regulation of the charge, a slag containing about 17% of pentoxide (P_2O_5) may be obtained. This slag fertilizer needs no further treatment except very fine grinding, but it is slow in decomposing, and the full effect is not obtained for two or

three years. It decomposes faster than ground phosphate rock, however, and has the important advantage of being cheap.

717. Bone Meal. Fertilizers are largely made from the waste products of slaughter houses, such as blood, bits of waste meat and other refuse, bones, hoofs, horns and hair. Bones are a very good fertilizing material, supplying both nitrogen and phosphorus, when used as raw bone—that is, without treatment other than grinding. But as a rule bones are extracted and then boiled, or extracted with steam under pressure to remove the fats and gelatine, after which the residue is ground and used directly for fertilizer as bone meal, the fineness of this “meal” having much influence on the rapidity of its decay in the soil. Being more spongy and soft, it yields phosphoric acid in a much shorter time than the hard “raw bone.” The latter contains about 22% of phosphoric acid, and 4% of nitrogen. But steaming reduces the nitrogen to about 1% while the proportion of phosphoric acid is raised to about 27 or 28%. Fine steamed bone yields all of its phosphorus in from one to two years, while the coarser, fatty, raw bone requires three to four years.

Raw bone contains on an average 22% of phosphoric acid, and about 4% of nitrogen. When boiled or steamed, part of the organic matter containing the nitrogen is extracted, reducing the nitrogen to 2 or 3% while the phosphoric acid is increased to as much as 28%, with an average of about 25%.

718. Use of Phosphoric Acid. Soluble phosphoric acid applied to the soil will unite with certain compounds of lime, iron or aluminum, or with some organic compounds and become fixed—either as the reverted or insoluble varieties—largely near the surface, and prevent the escape of the soluble form, thus differing from nitrates. Calcium, which is chemically more active than iron and aluminum, unites with the phosphoric acid to form tricalcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, if calcium is present; otherwise iron and aluminum phosphates are formed, the former being more available than the latter through subsequent decay.

719. Nitrogen Fertilizers. Nitrogen is the most expensive of the three elements used in fertilizers. This is because it is difficult to obtain it in a form that may be utilized by the plant, since most plants are not able to take it from the air. Nitrogen comes in three forms—organic matter, ammonia and nitrates.

Besides the nitrogen added to the soil by leguminous crops and barnyard manure, there are three sources from which the nitrogenous fertilizers are supplied,—namely, the slaughter houses, mines and artificial compounds of nitrogen made by chemical or electrical processes. The slaughter houses supply dried blood, tankage and bone meal. Blood is dried at a moderate heat and crushed to a powder between rolls. It contains about 10% nitrogen and is very uniform in composition.

720. Nitrogen from Organic Matter. All plants and animals contain nitrogen combined with other elements, and their value as a fertilizer depends upon the rapidity of the decay and the change of form, since the nitrogen must be supplied to the plant in a form that can be used readily. The following substances contain nitrogen in abundance, decay rapidly, and are very uniform in composition—dried meat, dried blood and concentrated tankage from slaughtering houses and rendering establishments, dried fish from fish oil and fish canning establishments, and cotton seed meal, which is the residue obtained after the oil is extracted from the seeds. These fertilizers are desirable where rapid and continuous feeding is required, and in light open soils, since they do not disappear as rapidly as ammonia and nitrates. The decay of the organic matter also helps to dissolve some of the mineral matter of the soil and to increase the available amount of phosphoric acid, potassium and calcium. Phosphoric acid is also furnished directly by these substances, more by fish and dried blood, and less by meat. Other less desirable sources of nitrogen are leather meal, wool waste, felt waste, etc.

721. Tankage is a substance obtained in the disposal of garbage. The garbage, containing fatty matter, is now collected

in many cities and subjected to a rendering process. It is put into steel digesters and is subjected to the action of steam at a pressure of 50 pounds for 8 or 10 hours, and the mass is reduced to a soft pulp. It is then put into presses and the oily matter pressed out, after which the press cake is broken up and dried in revolving steam-heated drums. Upon being powdered and sifted, it is used for filler in fertilizers under the name of tankage. It contains nitrogen, phosphoric acid and a little potash. On cooling, the oily matter forms a soft grease, which is used for soap and for candle stock. The water which is pressed out of the tankage with the grease contains an appreciable amount of ammonium salts and some potash. It is evaporated to dryness and the residue is mixed with the tankage, thus increasing the nitrogen and potash content of the latter. Bone meal has been dealt with in §717.

Tankage is also made from the waste portions of animals, steamed under pressure in tanks for the fatty matter contained in them. The amount of nitrogen and phosphorus varies with the kind of animal used and the proportion of the various parts. Five grades of tankage are sold containing the following percentages of phosphoric acid—18 to 19; 16; 13.5; 9 and 7. The percentage of the nitrogen is less as that of the phosphorus is more. It varies from 4 to 13%.

The approximate composition of the three substances in pounds per ton is shown in the following table:

	<i>Nitrogen</i>	<i>Phosphorus</i>	<i>Potash</i>
Dried blood . .	260—280	10—20	Traces
Tankage	80—240	30—120	Traces
Steamed bone meal	20—30	560—600	Traces

722. Fixation of Nitrogen by Bacteria. All plants require nitrogen compounds for food. It is a curious fact, however, that while they are surrounded by huge quantities of nitrogen, they cannot take it from the air. Growing crops gradually

absorb these compounds from the soil and they must be replaced to insure a good crop yield. As already stated this may be secured by adding artificial fertilizers, but the application of these is not always practicable for general farming on account of their high cost. It has long been known that some of the leguminous plants, such as beans, peas and clover will grow well in poor soil, and at the same time leave it with a richer nitrogen content. Investigation has shown that certain micro-organisms, known as "nitrogen fixing bacteria," living on tubercles on the roots of these plants, (Fig. 159) have the power

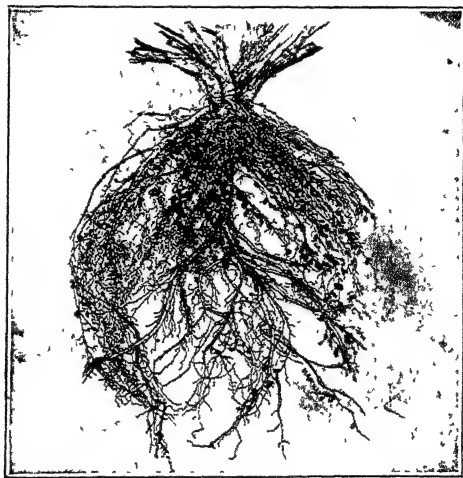


FIG 159. Roots with Nodules, Carrying Nitrifying Bacteria.

to cause the free nitrogen of the air to combine with other elements. These compounds are partly absorbed by the plants and the remainder is left in the soil, and thus enriches it. The modern farmer makes use of this fact by sowing clover on a field, and after removing one or two crops plows a crop under in the fall, thus greatly enriching the soil.

which the nitrogen is derived is inexhaustible, the importance of the process is manifest, especially when the amount of natural nitrates is constantly diminishing and will eventually disappear entirely.

The reserve supply of Chile saltpeter is estimated to be about 335,800,000 tons. The content of sodium nitrate varies from 8 to 45%. The lower percentages are difficult to work and new methods will be required to obtain the entire yield. During the year ending June 30, 1920 the consumption of nitrate was about 2,000,000 tons. Over 50% of this was used in the United States. The total capacity of the plants furnishing nitrate is estimated as about 4,000,000 tons; but probably the actual capacity is not more than three-fourths of that amount. The average price is now about three cents a pound.

The existing deposits of sodium nitrate will probably provide for all the requirements of the present century. Five hundred thousand Kg. of iodine are exported annually as a by-product.

Natural deposits of potassium nitrate have recently been reported as occurring in the northwestern part of Cape Colony and Transvaal. It occurs in shale beds covering several hundred square miles and is from 10 to 30 feet thick. The nitrate content is not less than 3% of the weight of the shale and varies up to 30%. Some of the lumps of crude nitrate, vary from 50 to 90% pure potassium nitrate.

725. The Fixation of Atmospheric Nitrogen, or the manufacture of nitric acid and nitrates from the elements of the atmosphere, water and limestone, was one of the problems presented to the chemists a few years ago when it was seen that the supply of sodium nitrate, or Chile saltpeter, would be exhausted in a few years. There are several processes, differing in detail, but all fundamentally the same, viz., the combination of the nitrogen and oxygen by means of powerful electric sparks.

The Birkeland-Eyde Process uses a large alternating current disc flame enclosed in a special iron furnace lined with fire clay

bricks. The electrodes are thick copper tubing $2\frac{1}{2}$ inches in diameter, through which water passes to cool them, (Fig. 161) and are capable of taking up 1500 horse power, giving a flame 1.8 meters in diameter. The electrodes last from 400 to 500 hours and must then be replaced. The temperature produced is from 3000° to 3500° and the temperature of the escaping gases is from 800° to 1000° . From 26,000 to 28,000 liters of air pass through each furnace every minute.

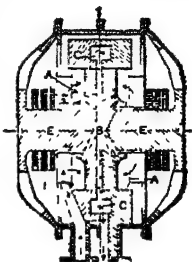


FIG. 161. The Birkeland-Eyre Process of Nitrogen Fixation.

In the *Schönherr Process* the arc is produced inside an iron tube of comparatively small diameter. The lower end of the iron tube contains a copper electrode, pierced through its axis and cooled with water. Through this passes an iron bar which can be thrust forward as needed, and which constitutes the

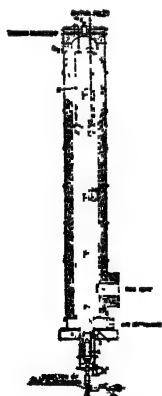


FIG. 162. The Schönherr Process of Nitrogen Fixation.

real electrode. Air passes into the tube through several series of openings situated one above the other and regulated with a movable sleeve which gives the air a rotary motion. The arc burns as steadily as a candle flame. The incoming air is heated to 500° by the outgoing gases. With 750 horse power, 40,000 cubic feet of air are used per hour, using an arc more than 20 feet long. The gases leaving the tube contain about 2% nitric oxide. See Fig. 162.

In the *Pauling Process* the arc is produced between two >< shaped electrodes. The arc is produced at the narrowest point, where the distance between the points is about 40 millimeters. Owing to the heated gases the arc tends to move upward, but the alternations of the current constantly re-form the arc at the lowest point

The air, previously heated enters between the electrodes at high speed, and broadens the arc to about 1 meter. The gases leave at a temperature of 700° to 800° and contain about 1.5% nitric oxide.

The following table shows the comparative yield of the three processes:

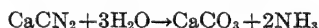
<i>Process</i>	<i>Grams of HNO₃ per K. W. Hour</i>	<i>Percentage of nitric oxide</i>
Pauling	60	1-1 5
Birkeland-Eyde	70	2
Schönherr	75	2 5

The nitric acid produced by these processes is used chiefly for the production of nitrates for fertilizing. Nitrate of lime or calcium nitrate is made by the action of the acid upon limestone, the product varying in color from red-brown to black. It contains approximately 13.1% of nitrogen, corresponding to 77% $\text{Ca}(\text{NO}_3)_2$, with 21.5% water, and 1.5% iron oxide, aluminum oxide, etc. Other products are sodium nitrite, sodium nitrate and ammonium nitrate.

726. Another Source of Combined Nitrogen is calcium cyanamide, or nitrolime, CaCN_2 . It is made by the action of nitrogen on calcium carbide at high temperatures, the equation being



When this product is treated with hot water or superheated steam the nitrogen is split off as ammonia



This is sold for fertilizing under the name of nitrolime. The action in the cold soil is probably more complicated than that shown, but it is a valuable source of nitrogen. It contains 20 to 22% of nitrogen. About 50,000 tons are used in the United States annually. See Fig. 163.

Calcium cyanamide may be produced by heating finely divided phosphate rock with an excess of carbon to about 1200°,

passing producer gas through the mixture to drive off the phosphorus and to form carbon monoxide in the residue. The temperature is then raised to 1500° , more producer gas is passed and calcium cyanamide, CaCN_2 , is formed.

When calcium carbide is mixed with a gaseous contact agent such as HCl or CCl_4 and is heated in the presence of nitrogen to form calcium cyanamide the presence of the contact agent causes the reaction to occur at a lower temperature.

727. Nitric Acid from Air and Illuminating Gas. Combined nitrogen may be produced by exploding a mixture of air and hydrogen or illuminating gas in a bomb holding 100 liters. Better results are obtained if some oxygen is added. Without the oxygen from 9 to 12 grams of nitric acid may be made per cubic meter of exhaust gas. With the oxygen this increases to 18 grams. The pressure is 3 to 4 kilograms per square centimeter.

728. In the Bucher Process no electric current is required. Soda ash and powdered coke are mixed together and powdered iron or iron ore is added as a catalyzer. The mixture is placed in a furnace and heated while air is passed over the mixture. Sodium cyanide is formed by the combination of the sodium of the soda ash, the carbon of the coke and the nitrogen of the air. When the waste carbon dioxide from the furnace is passed into a solution of the sodium cyanide, urea is formed. This has the formula CON_2H_4 . Urea has approximately 46.6% of nitrogen as against about 16.5% of nitrogen in sodium nitrate and 21.2% in ammonium sulphate. Urea is freely soluble and does not form acids in the soil. The sodium cyanide may be separated

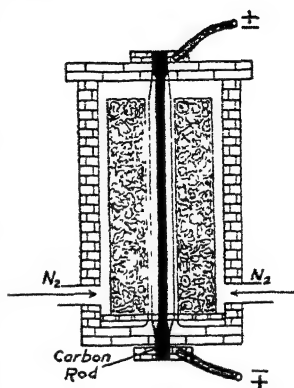
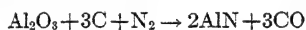


FIG. 163 Cyanamide from Calcium Carbide and Nitrogen.

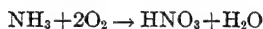
by the electric current into metallic sodium and cyanogen, C_2N_2 , the latter product being converted into oxamid, $C_2O_2N_2H_4$, by further treatment giving a powder nearly insoluble in water, and hence suitable for the slow evolution of nitrogen in the soil, the percentage of nitrogen being nearly 32.

729. In the Serpek Process nitrogen is passed over a heated mixture of aluminum oxide and carbon, forming aluminum nitride according to the equation

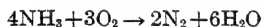


The action begins at about 1100° , is active at 1500° , and violent at 1800° . The temperature is not raised above 1850° because at about 2000° the nitride begins to decompose.

730. The Ostwald Process first forms ammonia by passing steam over nitrolime as shown in §726. The ammonia, mixed with air, is passed over a catalytic agent such as platinum covered with platinum black, which theoretically forms nitric acid according to the equation



But usually other products are formed unless great care is taken in the process, one reaction being shown by the equation



It has been found that a mixture of the oxides of thorium and cerium is much cheaper than platinum, and with care will give about 90% of the yield theoretically obtainable. Nitric acid produced by this process in Germany is of such purity that it is used in explosives.

731. Costs and Amounts Used. To produce one metric ton of nitrogen from the atmosphere by the various processes, the following powers are required: the arc process requires 60,000 kilowatt hours with no external fuel; the Haber process requires 2,700 kilowatt hours and 4,000 kilograms of coke; the Serpek process requires 9,700 kilowatt hours and 1,300 kilo-

grams of coal. The cyanamide process requires 16,900 kilowatt hours and no external fuel, except that used for producing the calcium carbide.

In 1920 the total production of combined nitrogen in the world was 671,300 tons. Of this amount Germany produced 420,000 tons from the air and 150,000 tons from by-product coke ovens. The British Empire produced only 12,800 tons, all in Canada.

732. Loss of Nitrogen. None of the sources of nitrogen can give all of the nitrogen to the plants, since, in addition to the loss by rainfall, which may be as high as 50%, denitrification, or the setting free of nitrogen, by certain bacteria, also occurs, particularly if very large quantities of horse manure are applied with the nitrate. The loss is sometimes all of the nitrate applied, and also some of the nitrogen of the soil formed by the nitrification of organic nitrogen. Again, ammonium sulphate is nitrified in the soil, and part escapes as gaseous nitrogen. Organic matter, which has to go through several changes to be available, may lose considerable nitrogen, since each change may be accompanied by loss. On the other hand the effects of nitrogen from ammonia and nitrates are practically all obtained the first year, while the effects of organic nitrogen continue for two or three seasons.

733. Sulphur and Borax. Where sulphur is used in fertilizers it is found to give increased yields, healthier plants, greater resistance to dry weather, the lessening or disappearing of certain diseases and makes the food materials more accessible.

Borax exerts a poisoning effect upon crops; as little as 6 pounds per acre showing signs of poisoning; while 8 to 10 pounds per acre produced injury to potatoes and 10 pounds per acre proved decidedly harmful.

734. High Grade Fertilizers cannot be made from low grade material. Sodium nitrate, ammonium sulphate, dried blood, superphosphates and potassium salts are standard products, and can be depended upon both as to composition and form.

The agricultural value of the soluble forms is greater than that of the insoluble forms, especially for immediate returns, but even so the application of fertilizer may not lead to profit, for if applied to low value crops the increase in yield may not pay for the fertilizer used, while the same applied to high grade crops may show a profit. In the best fertilizers the analysis will show the nitrogen present as nitrates or ammonia, the phosphoric acid as soluble, will show the derivation of the superphosphates, and the kind of potassium salt present.

735. Quantity Versus Quality. Fertilizer containing a large amount of good material may be worthless as a plant food, because it exists in an insoluble form, or is so difficult to decompose that the final value is small or slowly realized. The quality and amount of actual plant food determines the value, rather than the relative proportions, though for certain conditions that, too, is important. Since sodium nitrate furnishes about 16% of nitrogen; boneblack superphosphates about 16.4% of phosphoric acid; potassium chloride 52% of potassium; potassium sulphate 44.3% of potassium; and potassium magnesium sulphate 26.5% of potassium, it is a simple matter to compute the number of pounds of nitrogen, phosphoric acid and potassium in any mixture when the composition of the fertilizer is known. Since these are the active ingredients that give the value to the fertilizer as a plant food, anything added as a "make weight" does not add to the agricultural value of the fertilizer, but on the contrary reduces the relative amounts of the available fertilizing materials. The cost of freight and handling in the use of a cheap fertilizer is as great as when a good grade is used, and this added to the cost of the active ingredients usually makes the actual cost of a cheap fertilizer greater than that of a good one for the same fertilizing value.

736. Home Mixing of Fertilizers. Probably the most satisfactory method of using fertilizers where the user understands the principles of fertilization is to buy the unmixed fertilizing material, and then mix it for use, the proportions of

the different ingredients used varying with the different soils and the needs of the growing crops.

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CHAPTER XXX

TEXTILES

737. The more important textiles—wool, silk, cotton and linen are derived from different fibers; *wool and silk coming from animal fibers, cotton and linen from vegetable fibers*. Fig. 164 shows a comparison of these fibers.

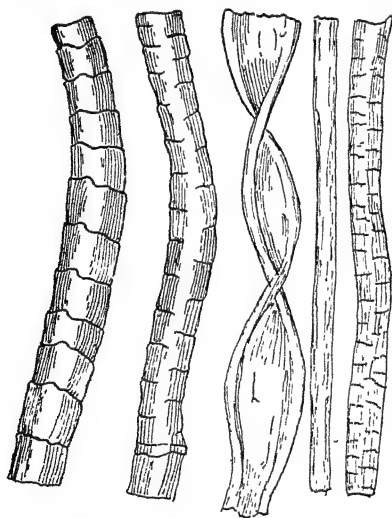


FIG. 164. Textile Fibers. 1 and 2, Wool; 3, Cotton; 4, Silk; 5, Flax

Silk is derived from the thread of the silk worm. This is made from a fluid formed in two glands in the body and exuded through two openings in the head of the caterpillar into a common orifice. The viscous streams there become coated with another secretion which flows from two other glands and become cemented together into a double strand. On contact with air the fiber coagulates. This coagulated fiber is wound around the cocoon which must be killed by heat or freezing in order to

secure an unbroken thread. Mulberry silkworms are the most common and yield the finest silk. The cocoon weighs from 1 to 3 grams, and of this $\frac{1}{6}$ is silk, of which $\frac{1}{2}$ can be unwound or reeled. The other half is usually combed or carded and afterwards spun.

738. Properties of Silk. The diameter of the silk fiber is from 0.020 to 0.025 mm., but wild silks may have a diameter varying from 0.040 to 0.065 mm. Silk is hygroscopic and loses 10 to 15% of its weight at 120° owing to loss of water. It is a non-conductor of electricity and may be electrified readily by friction. The fiber has a high luster and possesses great strength and elasticity. Silk has a central core of protein called *fibroin* constituting 70 to 75% of its weight, coated with another protein, the silk gum or *sericin*, 20 to 25%. There is also a small amount of waxy material and of coloring and mineral matter. The *sericin* may be removed by boiling with soap. The *fibroin*, which is not dissolved in water, is also insoluble in organic solvents, but is soluble in concentrated solutions of alkaline hydroxides, in mineral acids, in ammoniacal solutions of cupric oxide and nickel oxide, and in strong solutions of basic zinc chloride. The *sericin*, which is soluble in either a soap solution or in warm water, forms a jelly if even 1% is present. *Fibroin* and *sericin* differ from *keratin*, the protein of wool, hair, etc. by being free from sulphur.

739. Artificial Silks are made by several different processes. *Chardonnet silk* is made by dissolving nitrocellulose in a mixture of alcohol and ether, and forcing the solution through very fine openings, by means of great pressure, into warm air, the solvent being recovered later. It is subsequently denitrated, in order to render it less inflammable. This silk is extremely lustrous, but lacks strength, having after denitration, only about $\frac{1}{3}$ the strength of real silk, or $\frac{1}{2}$ the strength without denitration.

The *Wynn and Powell* method uses a solution of zinc chloride as the solvent for the cellulose, the solution being pressed into alcohol, which removes the solvent. The cellulose will be precipitated as filaments which may be dried and collected.

The *Despeisses-Pauly* method has the cellulose dissolved in ammoniacal solutions of copper salts, which are squirted into a solvent to remove the cellulose by precipitation. Copper car-

bonate in ammonia is used to dissolve the cellulose, and acid or alkaline solutions are usually used to precipitate the cellulose.

Other Methods make use of cellulose thiocarbonates. By spontaneous decomposition the cellulose is regenerated from such a solution and thrown out in an insoluble condition. This may take place immediately in the presence of suitable salts.

Cellulose esters, such as the acetates and formates, are also used but are more expensive. *Gelatin and casein* are used to some extent but not as much as the other materials.

740. Properties of Artificial Silk. The size of the filaments of artificial silk is from 3 to 12 times that of the real silk. The moisture content is about the same, but the artificial silks lose more strength when wet. The strength is said to be increased by treatment with formalin, CH_2O , which probably condenses the cellulose molecule. From 8,000 to 10,000 tons of artificial silk are produced annually, while the production of real silk is about 50,000 tons.

741. Wool is obtained from sheep, and grows as modified hairs. The wool contains a certain amount of wool fat, to protect it from mechanical injury and matting, and also dried perspiration. The dried perspiration is soluble in water, and the mixture of potassium salts that may be recovered in this manner is known as sudorate of potash, or *potassium sudorate*, and of this raw wool contains about 8%.

Wool fiber is composed of protein, known as keratin, found also in hair, horn, whalebone, feathers and egg membrane. The average composition of wool keratin is carbon, 51%; hydrogen, 7%; oxygen, 21%; nitrogen, 17%; sulphur, 4%. Keratin is probably a mixture of proteins. Wool contains from 1 to 2% of mineral constituents, and scoured wool contains 13 to 14% of water.

742. Properties of Wool. A 5% solution of boiling sodium hydroxide dissolves wool very readily, but strong sodium hydroxide, having a specific gravity of 1.4 to 1.5, does not dissolve the fiber, but causes it to become white and lustrous.

easier to dye, and about 30% stronger. This process is known as mercerization, and the wool is known as mercerized wool. A large proportion of the sulphur is removed by the process. Wool is completely disintegrated by strong mineral acids, but the dilute acids have not much effect upon it. Nitric acid causes a permanent yellow stain to appear, and this is known as the xantho-proteic reaction. (See §135) Sulphuric acid does not affect wool, but does destroy cotton and other vegetable fibers, thus permitting the quantitative determination of the cotton that is often mixed with wool. Wool is only slightly affected by dry chlorine, but is decomposed by the moist gas. It absorbs chlorine from weak solutions, loses its felting properties, becomes unshrinkable and has greater color combining power.

743. Shoddy or Mungo. Woolen clothes that have been worn for some time may have holes here and there, and thin spots so that they do not look as well as they did when new, although there is almost as much wool in them. The old clothing is cut to pieces, the stitches are picked out and the pieces of wool are then picked to shreds by machines. These woolen shreds are woven again into cloth, although the fibers are considerably shorter than the original fibers. Most wool is mixed with cotton, and as there is a great difference in the ability of these two materials to take dyes, (see Chapter 31), the usual mixture is to make the *warp of cotton* and the *woof of wool*. The wool then covers the cotton sufficiently to hide any defects in the dyeing. When the clothes are again picked to pieces to make *shoddy* there is usually a great deal of cotton mixed with it and after the process has been repeated several times the material is useless. The cotton is often removed by a process known as carbonizing. The cloth is placed in dilute sulphuric acid which acts upon the cellulose of the cotton so that after it is dried at about 95° the cotton is disintegrated to a powder and the wool is practically unaffected.

744. Cotton consists of the long hairs covering the seeds of the cotton plant, which grows as a shrub or small tree. (See

Fig. 165.) The cotton fiber is composed of a single hollow cell, and when unripe has the form of a long narrow tube. As it matures it becomes more or less flattened and presents the



FIG. 165. The Cotton Plant.

appearance of a narrow, somewhat opaque ribbon or band, with slightly thickened rounded edges. The fiber when ripe possesses a characteristic twist and the number of twists increases with the fineness of the fiber. Long fiber is $1\frac{1}{4}$ inches or more in length, medium is 1 inch, and short is less than 1 inch. The diameter of the fiber varies from 0.016 mm. in the fine Sea Island cotton to 0.021 mm. in the Indian cotton. Fig. 166 shows a cotton field.

745. Cotton Consists of about 90% cellulose, 7 to 8% water, 0.4% wax and oil, 0.6% nitrogenous substances and 1% mineral matter, or ash. The cotton wax is on the surface of the fibers and prevents the cotton from absorbing water readily. The wax is insoluble in water and caustic alkalis but is soluble in alcohol and ether. The oil of the cotton fiber is identical with the oil from the seeds. The ash consists chiefly of the phosphates, chlorides and sulphates of potassium, sodium, magnesium and calcium, with small quantities of iron and traces of aluminum.

746. Absorbent Cotton is made by boiling the cotton with dilute caustic alkalis under pressure to remove the wax and oil. It is then washed, treated with bleaching powder, and hydrochloric acid, again washed and dried.

Mercerized Cotton is made by treating the cotton with strong sodium hydroxide. The cotton acquires a silky luster. It is kept in a state of tension during treatment, or is allowed to shrink in an alkaline solution, and is afterwards stretched to its original length. This increases its power to absorb dyes. The flattened twisted fiber swells and is converted into the hollow cylindrical form. Mercerized cotton may be as high as 50% stronger than the unmercerized.



FIG. 166. A Cotton Field

Cotton is used as cloth, yarn, thread, etc. When treated with nitric and sulphuric acids it is made into gun cotton or collodion cotton, the latter forming collodion when dissolved in alcohol and ether. It enters into the composition of celluloid and is used in other ways.

747. Linen is the product of the flax thread and next to cotton is the most important vegetable fiber. The stalks are combed to remove the seeds and the leaves from the plant. The

stalks contain from 20 to 27% of fiber, and the rest is wood, pith, etc. They are fermented by steeping, or by treating with acids to remove the fiber, and are then washed, dried, and the woody portions are removed. The fiber is chiefly cellulose, averaging from $\frac{3}{4}$ to $1\frac{1}{2}$ inches long, and is about .002 inch in diameter, but a large number are united into a fiber bundle, varying from two to three feet in length. The impurities average 15 to 30%.

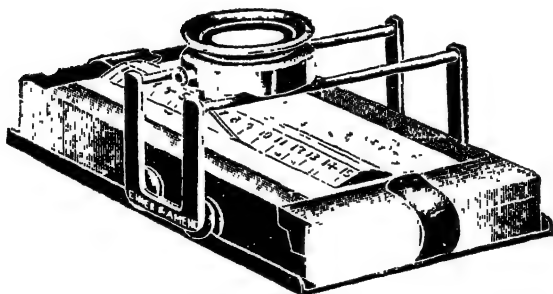
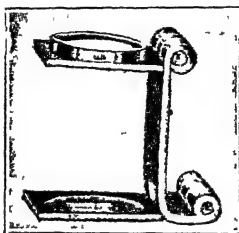


FIG. 167. Thread Counters; Pocket Type and Laboratory Type.

Linen is harder to bleach than cotton, but is more lustrous and tenacious, and less elastic. It is a better conductor of heat than cotton and therefore feels cooler. In general, linen behaves the same as cotton.

Since the cost of fine material is partly dependent upon the number of threads to the inch, great care is taken by buyers to determine the exact number. A laboratory type of thread counter is shown in Fig. 167 and a small pocket type is shown above.

748. Of the Other Fibers Used for Fabrics only brief mention will be given. *Cashmere wool* is produced by a species of goat of Tibet, the fibers ranging up to eighteen inches in length. *Mohair* is derived from the wool of the Angora goat and possesses great luster. It is produced chiefly in Turkey and in the Cape of Good Hope. *Alpaca* is derived from the hair of the llama and camels' hair from the hair shed by the camel. Other available fibers are *hemp*, derived from the hemp plant, used chiefly for ropes, sacking and canvas; *jute* from various species of *Corchorus*, grown in India, Turkey and Asia Minor, is used for carpets and matting. *Ramie*, *Rhea*, or *China Grass*, is obtained in China, Japan and India, containing about 80% cellulose: the fibers being about 1 inch long and varying from .0016 to .0032 inch in diameter. It is easy to bleach, but difficult to dye without injury to the luster.

Kapok is a comparatively new vegetable fiber from a plant found in the West Indies, South America and the Soudan. The threads are a clear yellow, somewhat silky and from $\frac{1}{2}$ to $\frac{3}{4}$ inch in length. They form hollow cylinders with thin walls, and since they are filled with air are very light. Owing to the waxy covering they are water proof, and are used for stuffing cushions, making life preservers, etc. The fruits are filled with seeds. These are separated from the fibers in special machines. The fibers are disintegrated, blown apart, brushed out and then heated enough to curl them, so that they may be matted together and converted into sheets.

749. Fire-proofing of Textiles is often necessary. Various formulas have been worked out, the fundamental principle being to impregnate the fibers with certain salts that will prevent the combustion of the fibers, without injuring the material or spoiling its appearance. The goods are either soaked in the fire-proofing solutions or are coated by use of a brush as in the fire-proofing of stage scenery, etc. The following solutions are some that have been used for this purpose:

(1) Ammonium sulphate, 8 parts; ammonium carbonate, 2.5 parts; boric acid, 3 parts; borax, 1.7 parts; starch, 2.07 parts; water, 100 parts. The mixture is boiled until all of the ingredients have dissolved, and the material to be fire-proofed is boiled in the solution, and then dried.

(2) Boric acid, 5 parts; potassium feldspar, 5 parts; gelatin, 1.5 parts; paste, 50 parts; water, 100 parts. This is to be applied with a brush.

(3) Equal parts of magnesium chloride, salt, and borax are dissolved in a little water to make a concentrated solution. It is applied in the same manner as the first solution given, and is very effective.

750. Waterproofing of Fabrics is accomplished by impregnating the fibers with rubber, rubber substitutes, or mixtures of various chemicals.

An efficient rubber substitute is made from rape or linseed oil, treated with sulphur chloride or carbon disulphide.

Chemical mixtures of various kinds are often very efficient. Copper ammonio sulphate will dissolve cellulose or gelatinize it. When this is evaporated on the surface of the fabric, a green varnish-like mass of cellulose, with copper oxide or a copper salt of some feeble acid derived from, and closely akin to, cellulose, coats the fibers, welding and cementing them together, and making the cloth waterproof. Copper ammonio hydrate alone, or with zinc ammonio hydrate makes an effective waterproofing material.

Cloth may be made non-absorbent of water, and hence practically waterproof by various other methods.

One formula is to dissolve 2 ounces of soap, and 4 ounces of glue in 1 gallon of water. The cloth should be boiled in this for several hours. It is then wrung out nearly dry, and placed in a solution of 13 ounces of alum and 15 ounces of salt in 1 gallon of water. It is finished by wringing, rinsing and drying.

Another formula calls for 2 pounds of dextrin, and 1 pound of white soap, dissolved in 1.6 gallons of water. The cloth is

boiled in this for some time, and is then treated with a second saturated alum solution, or one containing 6 pounds of zinc sulphate in 9 gallons of water.

Another method is to saturate the cloth several times alternately with solutions of aluminum sulphate and lead acetate.

An invisible waterproofing mixture contains isinglass, alum and soap, dissolved in water. This is applied with a brush, and should be rubbed in well. When dry it should be brushed on the wrong side, rubbing against the grain, then brushed with a little water and rubbed down smooth.

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CHAPTER XXXI

DYEING OF COTTON, LINEN, SILK AND WOOL

751. Dyeing Consists in imparting color to the substance of various materials, usually textile fabrics, in such a manner that it is not easily removed, or altered, if exposed. In *textile printing* the color is applied to portions of the material only, thus producing a pattern, but in other respects the operations are essentially the same. While dyeing is of prime importance in the textile industry, many other substances may be dyed, such as leather, ivory, horn, wood, straw, feathers, etc.

The Behavior of the Different Materials Toward Dyestuffs depends largely upon the nature of the material. In general it may be said that silk and wool, together with other animal products, behave in a very similar manner, while cotton, linen, and other vegetable materials act usually in an entirely different manner. Different dyestuffs, also, act in different ways towards the same material, so that both the material and the dye must be considered in all questions of dyeing.

Dyeing is often considered to be purely a physical process, but in the dyeing of silk and wool it is known that chemical action occurs.

752. Classification of Coloring Matters. From the practical standpoint of the dyer the various coloring matters may be divided into (1) mordant dyes; (2) acid-mordant dyes; (3) acid dyes; (4) direct dyes; (5) basic dyes; (6) sulphide dyes; (7) vat dyes; (8) ingrain dyes. The chemical classification of dyes is based upon the presence of certain groups of atoms, upon the integrity of which the coloring power of the dye depends, the group being known as the *chromophor*. The structures of some of these color groups are shown in Fig. 168.

753. Essential Properties of a Dye. A direct dye must possess color of considerable intensity and permanence, and must be capable of fixation to the fibers without injury to either fibers or dyestuff. A mordant dye need not be strongly colored, and may even be colorless, the color being developed by the mordant. Vat dyes, such as indigo, are usually insoluble in water and cannot be applied by ordinary processes, but their reduction products are soluble in alkaline solutions, and upon this depends the method of application. All dyes must possess permanency of color and be able to resist washing, and other influences, such as perspiration, strong sunlight, soap, etc.

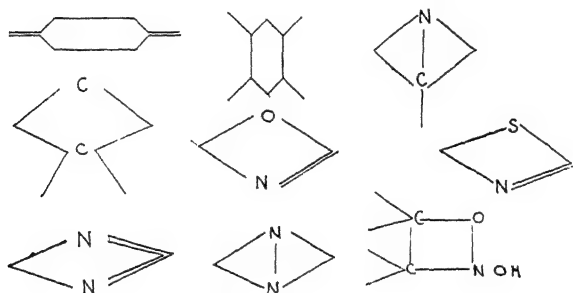


FIG 168. Chromophors.

754. The Dyeing of Wool. A greater variety of colors may be applied to wool than to any other kind of fiber. The most important dyes for wool are the mordant, acid-mordant, acid and direct dyes. In boiling solutions the affinity of wool for dyestuffs is greater than that of silk, but below 60° the affinity is frequently reversed. As a general rule the processes applicable to wool are entirely unsuited to cotton and it is possible in mixed fabrics to dye the threads of one and leave those of the other untouched. Fine wools usually require a larger amount of dyestuff to produce the same shade than the coarser varieties. Sometimes the affinity of wool for a dye may be increased by the addition of acids, alkalies, or oxidizing agents, such as

bleaching powder or hydrogen peroxide, or may be diminished by treatment with tannic acid solution or in other ways.

755. The Dyeing of Silk. In general the dyeing of silk is similar to the dyeing of wool, but the colors are usually less permanent. The acid, basic and direct dyes are the ones chiefly used, but the mordant and vat dyes may be used, though they tend to detract somewhat from the brilliant luster and suppleness on which the beauty of silk depends. The maximum absorption usually occurs at 60° to 80° and not at 100° as for wool. For dyeing black silk, chestnut extract or other tanning matter is used. The silk is dipped first into this solution and then into a solution of basic ferric acetate or ferric sulphate, and the process repeated until sufficiently weighted, and then dyed with logwood extract. Artificial silks are chemically more closely connected with cotton, and resemble cotton in dyeing. The varieties produced from collodion are dyed more readily than cotton or the artificial silks that are produced from cuprammonium or zinc chloride solutions.

756. The Dyeing of Cotton and Linen. Until 1884 turmeric, safflower and annatto were the only dyes that would dye directly upon cotton. In that year Congo red was discovered and since then there have been prepared a large number of synthetic dyestuffs that may be used for direct dyeing on cotton. The large class of acid dyes, useful in dyeing wool, cannot be used for cotton. Cotton has no affinity for metallic salts, and does not become mordanted by boiling in salt solutions. Cotton fiber has, however, a strong affinity for tannic acid in solution so that by boiling the cotton in tannic acid it may then be possible to apply a metallic mordant or basic dyestuffs to the fiber. Vat dyes are used for cotton and produce fast colors. The ingrain dyes are used almost exclusively on cotton. These dyes are produced directly upon the fibers of the cotton by precipitation. Mercerized cotton has essentially the same dyeing properties as ordinary cotton, but special precautions have to be observed on account of its great affinity for the direct dyes.

The Dyeing of Linen is similar to the dyeing of cotton but is more difficult probably due to the different physical structure of the fiber.

757. Miscellaneous Substances. *Jute* behaves to a certain extent like tannin-mordanted cotton, and may be dyed with the ordinary direct dyes, and also with the basic coloring matters without the aid of a mordant. *Leather* resembles wool in its dyeing properties, but is more difficult because only lukewarm solutions may be used, since hot solutions destroy ordinary leather, although chrome leather will withstand boiling water. The acid and basic dyes are chiefly used, and the mordant dyes to some extent. *Feathers* naturally resist water, owing both to their structure and to the grease present, and are, therefore, difficult to dye. Feathers behave like wool, and the acid, basic, direct or mordant dyes may be used, the reds, browns and blues being ordinarily dyed with acid dyes. Dyeing must continue for some time at a boiling temperature. *Straw* is difficult to dye on account of the large amount of silica present. It should be steeped for several hours in warm water before dyeing, and for colors the direct cotton and basic dyes are used, while blacks are obtained with logwood and iron. *Horn* may be dyed by the use of strong solutions of acid dyes; *ivory* by both acid and basic dyes; and *wood* by direct and basic dyes. Different methods of treatment have to be used according to the material.

758. The following table shows the common mordants and their uses:

<i>Mordant</i>	<i>With Cotton</i>	<i>With Wool</i>	<i>With Silk</i>
<i>Chromium Salts</i> Potassium dichromate $K_2Cr_2O_7$ or Sodium dichromate $Na_2Cr_2O_7$	Not used as mordants May be used to develop color by oxidation Such chromium salts as chrome alum, chromium bisulphite, chromium acetate, or sodium chromite may be used	Use a 3% solution. Add 1% H_2SO_4 , 1-5% HCl, 6% tartaric acid, or 1 to 2% formic acid to produce brighter colors. Boil for 1 to 1½ hours.	Not generally used with silk, but if used, tartaric acid must be added, but not H_2SO_4 , nor is it used alone.
<i>Aluminum Salts</i> Aluminum sulphate $Al_2(SO_4)_3 \cdot 18H_2O$ or Alum $K-Al_2(SO_4)_4 \cdot 24H_2O$	Goods are soaked, dried then passed through hot solution of sodium phosphate, arsenate or silicate, or ammonium carbonate. Or impregnate cotton with cold neutralized sulphated oil or tannic acid. Dry and steep in aluminum acetate or basic aluminum sulphate. Basic aluminum acetate also used, since the more basic the aluminum salts, the more readily do their solutions precipitate by heating or by diluting with water.	Use an 8 to 10% solution with 3 moles of potassium bitartrate to 1 mole of the aluminum salt. Boil 1 to 1½ hours; or use more expensive aluminum tartrate. Sometimes oxalic acid or potassium binovalate is used to add to the effect of the aluminum salt.	Boil with dilute aluminum sulphate, or steep for 24 hours in concentrated solution. Then wash.
<i>Iron Salts</i> Ferric sulphate $Fe_2(SO_4)_3$ Basic Ferric sulphate, $Fe_2(SO_4)_3 \cdot (OH)_2$	Usually a solution of some cold tannin matter is used first, then material is passed through a dilute solution of ferrous acetate, sulphate or nitrate. The cotton may alternately be impregnated with ferrous or ferric acetate, dried, and exposed to a warm moist atmosphere and finally fixed by passing through a hot solution of sodium phosphate.	A 7% solution with 4% potassium binovalate, but not often used.	 Steep in solution having a sp gr of 1.25 for 1 hour. Squeeze and wash. Repeat 7 or 8 times. Then boil in old soap bath and wash.
<i>Tin Salts</i> Stannous chloride $SnCl_2$ or Stannic chloride $SnCl_4$	Steep with a tannin, e.g. sumac, for three hours, squeeze and steep in stannic chloride (sp gr 1.02) for 1 hour and wash.	Boil in a solution of stannous chloride using 6% of the amount of the wool and 6 to 10% potassium bitartrate. An excess gives harshness.	Treat the same as wool or steep in a solution of stannic chloride for several hours.

<i>Mordant</i>	<i>With Cotton</i>	<i>With Wool</i>	<i>With Silk</i>
<p><i>Tannic Acid</i></p> <p>Gall nuts, sumac, for light colors</p> <p>Myrobalans, divi-divi, quebracho and chest-nut for dark colors</p>	<p>Tannic acid in a cold solution is absorbed by cotton, and if the cotton is immersed in a solution of a basic coloring matter the tannin combines with the base and a colored lake is formed. Better results if the cloth is passed through a solution of tartar emetic or stannic chloride, fixing the acid, giving tin or antimony tannate both of which have great attraction for the coloring matter, forming almost insoluble double tannates of tin or antimony and the color base. These are insoluble in alkaline solutions and therefore fast to soap.</p>	<p>Not used because fibers act as acid material</p>	<p>Not often used, but if used adds about 25% to the weight and gives black with iron mordants</p>
<i>Fatty Acids</i>	<p>Not used directly on cotton, but as their alkalies—soaps. Impregnate the cotton, dry; steep in cold solution of aluminum sulphate and wash. Gives an insoluble aluminum soap. Gives brighter colors when passed into solutions of basic coloring matter than when tannic acid is used, but not so fast to washing.</p>		
<i>Sulphated Oil</i>	<p>2 parts of castor oil and 1 part of sulphuric acid are allowed to stand 24 hours. Wash in salt solution to free from excess of acid and then neutralize with sodium hydroxide or ammonium hydroxide. Acts as a fatty acid and gives an extremely soluble soap with alkalies. Or use castor oil soap—castor oil boiled, with sodium hydroxide, the resulting compound being known as Turkey red oil, alizarin oil or soluble oil. Used in Turkey red dyeing.</p>		

759. General Methods of Applying Dyestuffs. *Mordant Dyes*, including the following natural dyestuffs: logwood, madder, cochineal, limawood, camwood, fustic, weld, quercitron bark and flavin; and the synthetic dyes such as alizarin, alizarin orange, alizarin maroon, alizarin blues, alizarin greens, alizarin black, anthracene blues, anthracene yellow, mordant yellow, naphthol green, caelestine blue, etc., are largely used in the dyeing of wool and in the dyeing and printing of cotton and silk. Generally they yield colors that have great fastness to light, soaping, acids, alkalies, bleaching agents, etc. They are now being replaced by the very fast vat dyes. When a fabric, previously mordanted with a metallic salt is dyed with a mordant dye a chemical reaction takes place resulting in the formation of a new compound which is the actual coloring substance, and this becomes fixed upon the fiber. There are three methods of application (a) the mordant may be first applied to the fabric and the dyestuff afterwards applied, known as the mordanting and dyeing method; (b) the order of application may be reversed, known as the dyeing and saddening method; (c) the mordant and dyestuff may be applied simultaneously, known as the single bath method. In the dyeing of wool the first process is usually preferable; the second process makes the matching of colors harder, and the third is applicable only when the color lake is soluble in dilute acids, such as the tin and aluminum color lakes. Mordant dyes are not used very largely on silk, chiefly because they detract somewhat from the luster of the fiber. With cotton the first process is usually followed, and aluminum is the chief mordant. Although a great many permanent and bright colors may be obtained with mordant dyes on cotton they are not very widely used, the fast colors being produced chiefly by the sulphide, vat and ingrain dyes.

Acid-mordant dyes are used largely on wool, and are suitable only for wool and silk. They are very numerous and are chiefly azo-compounds containing salicylic acid or orthoaminophenol compounds. Some however are pyrogallol or anthracene

derivatives. They include dyes giving a complete range of colors. In the dyeing of wool the usual method of application is to prepare a bath containing 3% sulphuric acid or 3 to 5% acetic acid and 5 to 10% of sodium sulphate. After the solution has been brought gradually to the boiling point, the boiling is continued until the coloring matter is entirely fixed, an additional amount of acid being added if necessary. Excess of acid, however, frequently retains the dyestuff in solution. The wool is then removed from the bath, the metallic salt is added and the wool is again boiled in the bath for half an hour. In most cases potassium dichromate to the extent of one-half the weight of the dyestuff is the mordant applied.

The acid-mordant dyes are of increasing importance in dyeing wool, but are little used on silk and not at all on cotton.

760. Acid Dyes, including azo-dyes, nitro-compounds, sulphonated basic dyes and phthaleins constitute by far the most numerous class of synthetic coloring matters. Of these the greatest number are azo-dyes. These contain few greens, blues and violets, but contain many reds, oranges, yellows, browns, and blacks. The nitro-compounds are few in number and are all yellows, the most important being picric acid and naphthol yellow. The greater number of sulphonated basic dyes are greens, blues and violets, and acid magenta. The resorcin, or phthalein dyes are chiefly brilliant pinks or reds, the eosins being the most important group. In most cases the commercial acid dyes are the sodium salts of sulphonic acids.

The simplest and usual method of dyeing with acid dyes is to prepare a bath containing the requisite amount of the dyestuff with 1 to 4% of sulphuric acid and about 10 to 20% of sodium sulphate. The wool is dyed in this solution for about an hour, boiling for the greater part of the time. The sodium sulphate exerts a leveling influence upon the fixation of the dyestuff, probably because of the solvent action it exerts. Another reason is that it exerts a retarding action upon the liberation of the free color acid by the sulphuric acid. Where level colors are not

readily produced the acid may be added gradually, or may be substituted by an ammonium salt, such as the sulphate or acetate. The soluble colored sodium salt is then changed very gradually to the insoluble free sulphonic acid

In dyeing silk the acid dyes are applied in a bath containing up to 25% by volume of "boiled off" liquor, the soapy solution of the silk gum obtained in removing the gum from raw silk. Sulphuric, acetic or formic acid is added and the bath is kept at a temperature of 80° to 90° since the silk has a greater affinity for the dye than has the wool. After dyeing, the silk is brightened by working in a dilute solution of sulphuric, acetic or tartaric acid, and dried without washing.

There is no satisfactory method of dyeing cotton with acid dyes.

761. Direct Dyes have the special property of dyeing cotton fabrics without the use of a mordant. They, too, are chiefly azo-dyes, but contain the $-N=N-$ group twice in the molecule and thus constitute the tetrazo-group of the azo-dyes. There are a great many of these dyes, and they are obtained in all colors, all of them being introduced since 1884. Primuline is an example of a direct dye that is not an azo-compound. It contains the group $\begin{matrix} \diagup S \diagdown \\ N \end{matrix} C-$. Turmeric is the only important natural direct dye for cotton. Direct dyes may be used on all fibers but are not used to any extent on silk.

In the dyeing of wool with the direct dyes the bath is made slightly acid and sometimes a small amount of sodium sulphate is added. Fastness is often improved by after treatment with a metallic salt, making the action similar to the acid-mordant dyes.

Cotton may be dyed in a cold, luke-warm or boiling solution of the dye, to which is added up to 2% of sodium carbonate and up to 20 grams per liter of sodium chloride or sodium sulphate. More concentrated solutions must be used if the bath is kept at a low temperature. Brighter colors are obtained if the dyed

material is passed through a solution of Turkey-red oil before drying or if this substance is added to the dye-bath. The color produced by the direct dyes upon cotton may or may not be the same as that produced upon wool when the same dye is used. Mercerized cotton has a greater affinity for direct dyes than the ordinary cotton fiber.

762. The Basic Dyes are not as numerous as the other groups but they contain the most brilliant dyes known, such as methylene blue, malachite green, methyl violet, auramine yellow, rhodamine pink, etc. The chemical composition of the basic dyes differs very widely, some being derivatives of di- or tri-phenyl methane, while some are azo-colors and some contain sulphur. Basic dyes are but little used on wool, since the acid dyes yield faster colors. Wool has, however, a great affinity for the basic dyes and a small amount of acetic or sulphuric acid is usually added when used.

Basic dyes are suitable for dyeing silk where fastness to light is not important. The silk yarn is dyed at 60° to 80°, some "boiled off" liquor or neutral soap being added to the solution of the dye.

Cotton has but little affinity for the basic dyes, so that when they are used a mordant must be applied. Tannin mordants have a natural affinity for cotton but the colors produced are not fast to washing. Faster colors may be produced by double mordanting, first with the tannin and then with a solution of a salt of antimony, tin or iron. Fatty mordants, such as Turkey-red oil or soap produce a brighter color but less fast. Mordant, sulphide, acid and direct dyes have an affinity for the basic dyes and hence may be used as mordants, compound shades being thus obtained.

763. The Sulphide Dyes, which have of late years been of increasing importance, are obtained as powders, that are usually insoluble in water, but are soluble in a solution of sodium sulphide. They are used chiefly for the production of fast

blacks upon cotton and other vegetable fibers but fast blues, greens, browns and yellows may also be obtained.

Sulphide dyes are rarely used on wool, because of the injurious action of the sodium sulphide upon the fiber. The blacks, blues and browns are used on silk, the dye being dissolved in the solution of sodium sulphide, with twice as much glucose as sulphide. This is boiled until the dyestuff is dissolved and is then added to the boiling dye-bath already containing 1 gram of soda ash, 3 cc. of Turkey-red oil and from 5 to 10 grams of sodium sulphate per liter. The silk is kept below the surface of the dye for an hour, then rinsed, soaped and brightened with acetic acid. Fastness may be improved by subsequent boiling in a solution containing 2 to 4% of potassium dichromate and 3 to 6% of acetic acid.

In the dyeing of cotton with the sulphide dyes, the necessary ingredients in the dye-bath, in addition to the dye-stuff are sodium sulphide, sodium sulphate or other neutral salt, and an alkali, usually sodium carbonate. The addition of Turkey-red oil, monopol oil or glue tends to produce more level and brighter shades. The exact proportion of the various ingredients varies with the color desired, but the baths are very concentrated so that the same bath is used over and over, the color being added as needed. The cotton is kept wholly immersed and dyeing takes place just below the boiling point. Some of the sulphide dyes do not require any after treatment except exposure to the air, but others have to be treated with oxidizing agents, such as chromium salts or hydrogen peroxide so as to insure complete oxidation. Potassium dichromate and acetic acid are also used extensively.

764. The Vat Dyes formerly were represented by indigo alone, but the synthetic production of indigo led to the discovery of a great many other dyes of similar nature, many being derivatives of indigo (indigotin), while some of the others are the alcole dyes, the cibanone dyes and the indanthrene dyes. While blues predominate, all colors may be obtained.

The essential features of a vat dye are its easy reduction to a form readily soluble in dilute alkali, its attraction in this condition by the fiber, and its rapid reoxidation on the fiber to the original insoluble condition. The reduced condition is termed the "vat."

In the dyeing of wool there are two chief indigo vats, (1) the fermentation vat and (2) the hydrosulphite vat. In the first the indigo is mixed with woad, bran, madder, lime and water, and the fermentation that sets in after warming the liquor changes the starchy matter into glucose, then into lactic acid, which then undergoes butyric fermentation with the evolution of hydrogen. In the hydrosulphite vat synthetic indigo is usually used. It is mixed with sodium hydroxide and sodium hydrosulphite solutions and water. The mixture is heated to 50° to reduce the indigo to indigo white, the solution becoming clear greenish yellow. After working the goods in the vat they are squeezed and are then exposed to the air to oxidize the indigo. Indigo vat blue is an extremely fast color, but has the defect of being liable to rub off. It is not employed to any extent on silk, but is used extensively on cotton, the chief difference being that it is applied cold.

Indigoids are closely related to indigo, and are made synthetically. They are of two classes, (1) where the central chromophor is $-\text{CO}-\text{C}=\text{C}-\text{CO}-$, the same as in indigo, and (2) where the central chromophor differs by the addition of 2 imino

groups, becoming $\begin{array}{c} -\text{CO} \backslash \\ \text{NH} \end{array} \text{C}=\text{C} \begin{array}{c} / \text{CO}- \\ \text{NH} \end{array}$. The indigo chromophor cannot be destroyed without changing the nature of the dye. The indigoids are vat dyes, the same as indigo. The imino groups may have a different position, or may be replaced by hydrogen, or other elements or radicals.

765. Ingrain Dyes are those coloring matters other than the mordant dyes which are produced from their constituent bodies upon the fibers. The ingrain dyes may be divided into (a) aniline black; (b) insoluble azo-dyes; (3) metallic dyes. Aniline

black is produced by the oxidation of aniline in acid solution by such agents as potassium chlorate and cupric chloride. There are many modifications of the process of oxidation and also of application, the dye usually being applied to cotton and not to animal fibers, although a mixture of silk and cotton for umbrella covers is often dyed by this dye.

The insoluble azo-dyes are used largely for silk and wool and have little affinity for cotton.

Of the metallic salts used for dyeing only one will be described. Iron buff is first produced by precipitating hydrated ferric oxide on the fibers, after which the material is passed into an acid solution of potassium ferrocyanide. The color, Prussian blue, is extremely fast to light but is sensitive to alkalis. It is little used on wool.

In general in the dyeing of mixed fabrics such as cotton and wool the operation may be conducted by selecting a dye that has affinity for both fibers, such as the benzidine dyes; or by dyeing first the wool in the usual manner with an acid dye, then mordanting the cotton with tannic acid and tartar emetic or stannic chloride and dyeing in the cold with a basic coloring matter.

Cross dyeing is produced by first dyeing the cotton warp, then weaving with wool and dyeing the latter by means of acid dyes.

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CHAPTER XXXII

SOAPS, LAUNDRY CHEMISTRY AND CHEMICAL CLEANING

766. A Soap may be defined as the salt of a fatty acid. There are, however, many varieties, but as a whole they may be divided into two classes—(1) the soaps of the alkali metals which are water soluble; (2) the soaps of the alkaline earth metals which are insoluble in water and are known as the metallic soaps.

767. The Alkali Metal Soaps are further divided into two classes (1) the soda soaps, which are hard, and (2) the potash soaps which are soft. The fatty raw material may be any oil or fat but not all of them are entirely suitable.

768. Hard Soap by the Cold Process. For this kind of soap the cocoanut oil group of oils and fats is the most suitable. The fat is stirred with concentrated sodium hydroxide solution having a specific gravity of 1.35 at a temperature of about 35°. The mixture is covered and allowed to stand for 24 hours. This soap usually contains an excess of either fat or alkali. Fats containing notable amounts of the free fatty acids are not suitable because of too rapid formation of the soap causing lumps. Castor oil is used in the cheap transparent soaps, and complete transparency may be obtained by adding sugar solution or sodium silicate solution.

769. Hard Soap by the Hot Process is better, yielding a soap of uniform quality, color and hardness, and containing the largest amount of glycerin. The oils and fats are introduced into the soap kettle and churned by steam. Dilute sodium hydroxide solution is run in (Fig. 169.) It is necessary to use an excess of the sodium hydroxide to insure complete saponification. A pasty mass is formed, and this soap paste is made into com-

mercial soap by the addition of salt, known as salting out. The materials separate into two layers, an aqueous layer of salt, glycerol, and the excess of sodium hydroxide, and the upper curdy mass of soap granules with 30 to 35% of water. The lower layer is drawn off and treated to recover the glycerin. The

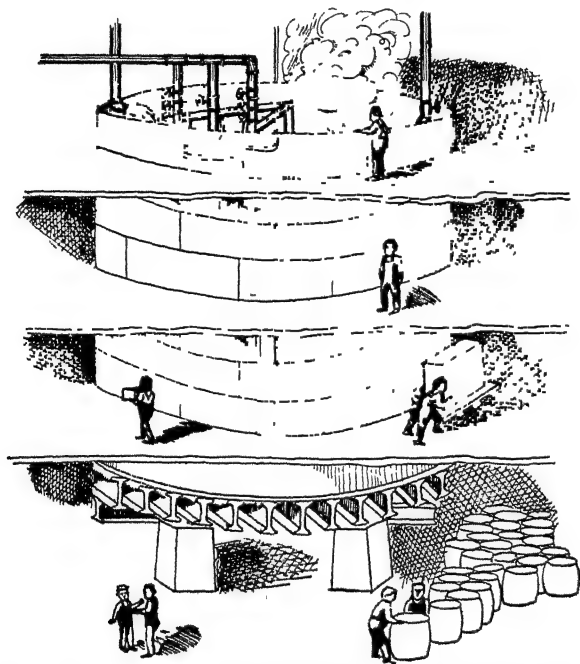


FIG. 169. Kettle Occupying Four Floors for Boiling Soap

soap granules are boiled with water and again with sodium hydroxide for complete saponification, and separated. The material is treated again the same way to remove the impurities and to improve the color. In some cases it is boiled with a somewhat concentrated solution of sodium hydroxide, and salted out again to a curd; then "fitted" by allowing it to stand for several days,

when the lowest layer will be aqueous, covered by a dark soap containing the impurities in the form of the iron and copper salts of the fatty acids, and an upper layer of "neat soap" in

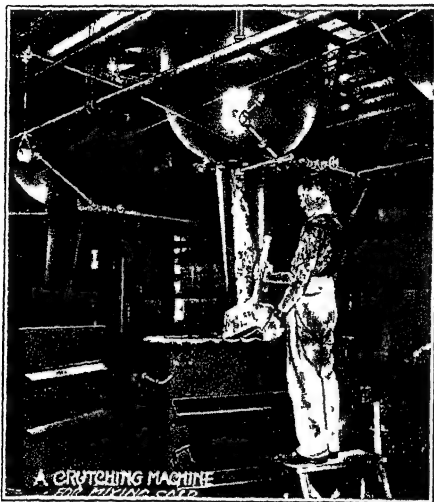


FIG. 170. Crutching Machine for Mixing Soap

which the excess of sodium hydroxide is very small. The soap is next run into crutching, or mixing, machines (Fig. 170), where the color and perfume are added if wanted. The soap is then run into frames for a few days to solidify. (Fig. 171.) The sides of the frames are then removed and the soap is cut, first into slabs, then into bars, and finally into cakes,

which are stamped, wrapped and sold. (Fig. 172.) Pure commercial soaps made in this way have 30% water and 63 to 64% fatty acids and the rest as combined sodium oxide.

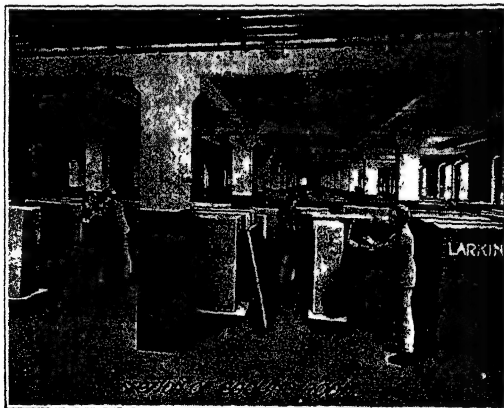


FIG. 171. Cooling the Soap.

770. In Mottled Soaps part of the iron and copper soaps present as impurities are not

thoroughly separated and segregate on cooling as veins in the soap. Mottled soaps contain about 61% of fatty acids. They may be adulterated with salt, sodium carbonate or sodium silicate to any desired extent, and may contain as low as 10% of fatty acids. Adulteration is excused by the manufacturers by saying that it makes the soap harder and a better cleanser. If soap contains from about 52 to 60% of fatty acids it is known as *filled soap*. It is called *loaded* when it contains clay, talcum, barium sulphate, asbestos, seed husks, starch, etc. If there is less than 50% of fatty acids the soap is called *adulterated*.

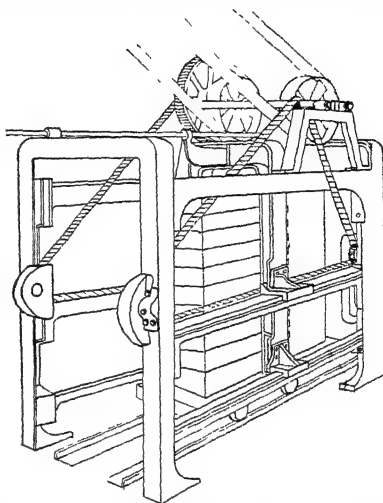


FIG. 172. Slabbing and Cutting the Soap.

771. Soft Soaps are easier to make than the hard soaps. The fatty substances are boiled with potassium hydroxide and there is no salting out. Potassium carbonate is required to produce a clear translucent soap of good consistency. The soft soap may be made in fire heated or steam heated vessels. Linseed oil is used in the best soft soaps, and the mixture is churned with steam. Potassium hydroxide is added, and when the entire mass is slightly alkaline the potassium carbonate is added in solution. The excess of water is removed by heating with a closed steam coil while the soap is agitated to expose it to the air. If cottonseed or corn oil is used the soap becomes dull in frosty weather. All glycerol is retained in the soft soap and some excess of potassium hydroxide and potassium carbonate. The retention

of the glycerol adds to the transparency. Rosin may be used in soft soaps the same as in hard soaps, and lowers the value.

Laundry soaps are settled or mottled tallow rosin soaps.

Toilet soaps if of good grade may contain as high as 80% of fatty acids, but there are many cheap grades, the inferiority being concealed by coloring matter and perfumes. Fig. 173 shows a milling machine for toilet soaps.

Floating soaps contain air incorporated with the soap while it is in a pasty condition.

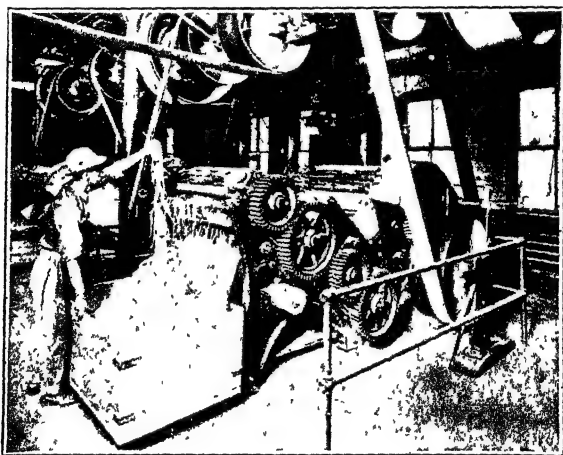


FIG. 173. Milling Machine for Toilet Soap.

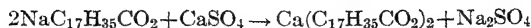
Medicated soaps contain medicinal substances incorporated with the soap.

Disinfecting soap or antiseptic soap contains carbolic acid.

Soap powder consists of a mixture of hard soap and sodium carbonate.

Dry cleaning soap and soap emulsions contain neutral Turkey-red oil and caustic alkali together with carbon tetrachloride and chloroethylenes.

772. When Soap Is Used with Hard Water, the general reaction may be represented by the equation



The soap cannot form an emulsion with the oily material on the skin until after it has reacted with the calcium salts, so that the use of hard water for washing purposes is an expensive process. After the soap has formed the emulsion with the oil, the dirt can be easily removed. Warm water makes the emulsifying process more rapid and more thorough, so that the dirt is removed more easily by using warm water rather than cold. The calcium stearate formed when the soap reacts with the hard water is a sticky, gummy substance appearing as whitish masses in the water. Unless removed from the basin when soft they form a hard crust, difficult to remove.

Soap Substitutes. A French patent gives as a substitute for soap a mixture of soap lyes, with about 15% by weight of cornmeal, and if desired about 15% kaolin. The mixture is heated to about 80° to 90°, and when cool has the consistence of a thick white cream, and possesses to a high degree the properties of a water-soluble soap of good quality.

773. In the Laundry the chief cleansing agents are water, soap, the carbonates and bicarbonates of both sodium and potassium, sodium hydroxide, borax, and mixtures that are sold as washing powders, or washing sodas. The alkalies react readily with wool and silk, but not with cotton or linen unless concentrated, although they will produce a yellow color, even if weak. Soap for laundry use should be made from good grades of red oil—crude oleic acid. This will produce a soap that is more soluble than tallow soap and makes a better cleanser than soaps made from the stearates and palmitates. Rosin soaps are inferior and produce a yellow color if used repeatedly. Soap breaks up the fatty film, wets the oily surface and lubricates the particles of dirt. It probably forms an emulsion with the fat and

although there are several theories concerning the action of soap the exact nature of its action is not known.

774. Goods Washed in the Laundry may be classified into (1) white collars, cuffs and shirts, either cotton or linen; (2) colored cotton, usually sorted as to colors; (3) woolen goods; (4) white goods other than cuffs, collars and shirts; (5) silks. The method of treatment is different with the different kinds of goods and the description given will be for collars, cuffs and shirts.

775. The Treatment for Collars and Cuffs consists of (1) cold rinse at the room temperature for 5 minutes; (2) first suds, brought to a boil in 10 to 15 minutes, and continued for 10 minutes longer; (3) second suds and bleach, applied as the first suds; (4) warm rinse at 60° to 80° for 5 to 10 minutes; (5) same as (4); (6) warm rinse and acid at 40° for 5 to 10 minutes; (7) blue, at 40° for 5 to 10 minutes; (8) rinse at 40°, for 5 to 10 minutes; (9) same as (8).

776. The Water Used in the laundry should be a natural soft water or a softened water. (See §772.) Hard water should not be used since it forms difficultly soluble soaps of calcium and magnesium, difficult to remove. These soaps are also deposited in the fibers of the goods and decompose on ironing into compounds that produce yellow or brown spots. The water softener used should leave the water nearly neutral. The reagents are added, and mixed by the use of steam, compressed air, or paddles. Alum is added as a coagulant to carry down the suspended particles. A sand filter is also very effective for purifying.

777. The Cold Rinse removes the loose dirt and dissolves the albuminous substances present, which would coagulate if the goods were placed in hot water at first. Usually a little soda ash or washing soda is added to the water.

778. The First Suds contain $\frac{3}{4}\%$ of soap and $\frac{1}{4}\%$ soda ash. Hot water is gradually admitted and steam is passed through to keep the temperature at the boiling point. About 30 gallons of water are used for 75 pounds of dry clothes.

779. The Second Suds are made a little weaker and the bleach is added. For this purpose sodium hypochlorite is used. It may be made by the action of soda ash and calcium hypochlorite, or by the electrolysis of a solution of common salt and may be prepared in the laundry. From 50 to 70 grams of available chlorine are necessary for 30 gallons, and this will be used up in from 10 to 30 minutes, and more must be added or the clothes will not be uniformly white. The bleaching is the most harmful part of the washing, since the chlorine weakens the fibers and the collars will break after 8 or 9 treatments, while a collar washed without bleaching may be washed 25 times without being any weaker than the bleached collar after 8 or 9 washings.

780. The Acid Rinse neutralizes the alkali used in the first part of the washing. Basic aniline dyes are added to remove the yellowness. The acid used is an N/50 solution of acetic, lactic or oxalic acid. The first two do not ionize readily, and are, therefore, called weak acids. They do not attack the cellulose fiber readily even if concentrated. Oxalic acid ionizes more completely and is a stronger acid. It is used more than the others because it removes the iron stains, forming complex ions of iron oxalate. The acid must be carefully removed before drying, since as the water is driven off the acid becomes more concentrated and the fibers are weakened. Sometimes sulphuric or hydrochloric acid is used instead of oxalic but they, too, are very strong. When cellulose fibers are boiled with an N/50 solution of oxalic acid for 3 hours the strength of the threads is diminished $\frac{1}{3}$. Enough acid must be added to neutralize the alkali or the blue does not set evenly and the alkali remaining causes the starch to change into dextrin and glucose in the ironing machines. The starch used is a mixture of wheat and corn starch boiled. The starch has been partially converted by acids until it forms a thin solution when boiled with water. A solution is made containing 100 grams per liter and the starch is rubbed in by a machine at a temperature of 65° to 70°. The excess of starch is wiped off, first with the hand, and then with a

piece of cheese cloth, care being taken to have the starch all through the goods in order to avoid splitting of the piles. They are then dried, dampened and ironed, first flat, and then shaped by a machine which irons the turns, etc.

781. Colored Articles are washed with less alkali and no bleach is used. Wool and silk are washed after the same general principles as colored goods, but sometimes a bleach is used. Chlorine cannot be used since it attacks the fibers and hydrogen dioxide is used instead, or a solution of sodium perborate or sodium hydrosulphite may be used.

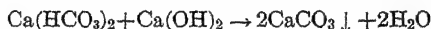
Further Applications of Chemistry to the laundry may be found in the analysis of the raw materials, testing soaps for adulterations, preparation of bleaching agents, blueing material, etc.

782. Chemical Softening of Hard Water. Although soap may be used to soften hard water, it is an expensive process. By using a standard soap solution the amount of hardness in water may be determined. It will be found that all hard waters require much more soap than soft water, and that in some forms of hard water 20 to 30 times as much soap may be required. It will be seen that the question of softening the water becomes one of great practical importance, especially in the laundry where so much water is used, and in steam boilers to prevent the formation of boiler scale. (See Fig. 110.)

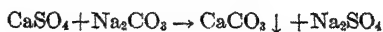
Calcium Bicarbonate, the chief ingredient of temporarily hard water, occurs widely distributed in nature as limestone, CaCO_3 . This is dissolved easily when carbon dioxide is dissolved in the water, forming the calcium bicarbonate



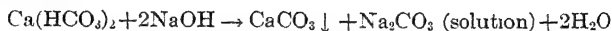
which is about thirty times as soluble as the carbonate. Calcium hydroxide, or slaked lime, $\text{Ca}(\text{OH})_2$, may be used to throw the calcium bicarbonate out of the solution, softening the water



When water contains calcium sulphate it may be softened by the addition of sodium carbonate



When the carbonate and sulphate are present the water may be softened by using sodium hydroxide which acts first upon the bicarbonate.



after which the sodium carbonate acts upon the calcium sulphate as above. If iron carbonate is present it too is held in solution as the bicarbonate and is precipitated by boiling.

Sodium carbonate also softens water containing the calcium bicarbonate, forming calcium carbonate and sodium bicarbonate,



Ammonium hydroxide will act upon either the carbonate or the sulphate, softening the water. Borax and soda do not bleach but prevent staining by the iron by precipitating the soluble iron bicarbonate as iron carbonate before the goods are put in.

783. "Dry" or Chemical Cleaning. The term "dry cleaning" is used to cover methods of cleaning where water is not used. It is *not a dry method* at all, and is, therefore, incorrectly named; chemical cleaning being what is meant. Chemical cleaning was introduced in France near the middle of the 19th century, by the use of camphene, a terpene used at that time for illuminating purposes.

The solvent chiefly used for chemical cleaning is petroleum benzine. Its specific gravity is about 0.78 and the boiling point varies from 80° to 120°. Benzine is highly inflammable and dangerous to use. The commercial product is apt to contain small amounts of carbon disulphide, thiophen and other sulphur products that impart a disagreeable smell to the fabrics. The presence of carbon disulphide in benzine may be detected by the formation of a precipitate when phenyl-hydrazine is added. The general method of cleaning is to beat out the loose dust and then immerse the article in the benzine, rubbing any spots that do not disappear readily. The garments are hung in a current

of air for 12 hours or more to remove the odor of the benzine. After the solvent has been used for a time it is full of dirt and grease and is distilled. This purifies the solvent and it may be used again. See Fig. 174.

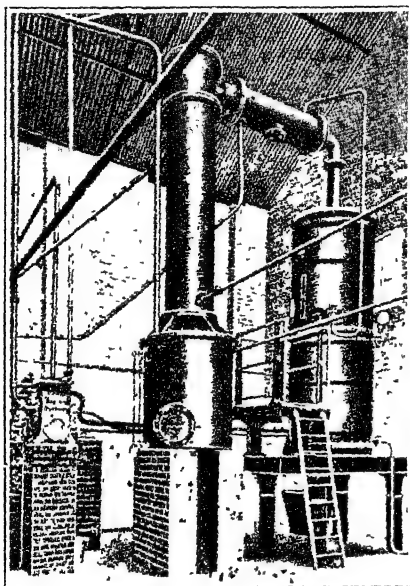


FIG. 174. Still Used by Dry Cleaners for Recovery of Solvent.

Special Soaps, soluble in benzine, are employed in chemical cleaning. They assist in the degreasing, and diminish the risk of fire. These soaps consist of practically anhydrous sodium or potassium oleate or stearate, made by melting together oleic acid and soap, or by dissolving the alkali in denatured alcohol and adding to the solution the required amount of oleic or melted stearic acid. Strong ammonium hydroxide may be substituted for the sodium or potassium alkali.

784. Substitutes for Benzine are now being used to a certain extent, but owing to their cost they are not as widely used as benzine. Among them are chloroform, CHCl_3 ; carbon tetrachloride, CCl_4 ; dichlorethylene, $\text{C}_2\text{H}_2\text{Cl}_2$; trichlorethylene, C_2HCl_3 ; perchlorethylene, C_2Cl_4 ; tetrachlorethane, $\text{C}_2\text{H}_2\text{Cl}_4$ and pentachlorethane, C_2HCl_5 . These noninflammable substitutes for benzine are all classed chemically as chlorine derivatives of methane, ethylene and ethane. On account of the cost carbon tetrachloride and trichlorethylene are used more than

the others. Carbon tetrachloride is often sold at a higher price as "Carbona."

785. The Removal of Stains, Grease, Ink, etc., from fabrics

BRIEF TABLE TO SHOW THE MANNER OF REMOVING
STAINS AND GREASE

Kind of Stain	From Linen	From Cotton	From Wool	From Silk
Sugar, glue, blood, albumen	Wash	with	water	
Grease	Soap, alkalis	Warm soap Chloroform.	Soap, NH ₄ OH Chloroform	Benzine, ether, egg, chalk, NH ₄ OH, etc.
Varnish and oil paint	Turpentine,	benzine	and soap	Benzine, ether, soap Rub with care
Stearin	95	per	cent	alcohol
Vegetable colors, fruit colors, wine	Sulphur dioxide, warm chlorine water	Warm soap suds and ammonia		Suds and ammonia, gently.
Aniline inks	Warm chlorine	water	Sulphur dioxide or ammonia with care	
Alizarin inks	Rather strong solution of tartaric acid		Weak tartaric acid if it does no harm	
Iron rust, iron ink	Oxalic acid, warm dilute HCl, citric acid, ammonium oxalate, etc	Citric acid 25% HF for a second, immediate rinsing repeated as required	Citric acid or dilute HCl, if the dye is neutral	Stain usually becomes worse no matter what is used
Lime or alkalis	Water	or	very dilute acids	followed by water.
Tannin, nut shells.	Javelle water dilute HCl, strong tartaric acid, etc	Wash alternately with water and dilute chlorine water if it does not affect the goods Chlorine is not good for either wool or silk		
Coal tar, wagon grease, etc	Soap, oil of turpentine, alternating with water Xylol	Lard, then soap, followed by alternate applications of turpentine and water Xylol.		Lard, soap, alternate benzine and water. Let water fall some distance No turpentine
H ₂ SO ₄ or HCl, (red stain)	Neutralize the acid by applying NH ₄ OH Then wash with water.			
HNO ₃ (yellow stain)	Nothing will remove the color. NH ₄ OH will make the color more intense			

When available, the non-inflammable and non-explosive chlorine derivatives, such as carbon tetrachloride, trichlorethylene, and chloroform, should be substituted for the explosive solvents, ether, benzine, carbon disulphide, benzol, petroleum ether, etc., which are used extensively for removing grease

depends upon the kind of stain and the nature of the fabric. Chemically the action may be one of neutralization, or it may depend upon the solubility of the staining material in some chemical used, or in forming an emulsion which may be washed out with water. The table on page 523 shows some of the more common methods used for removing stains, grease, paint, etc.

786. The Removal of Ink Stains often causes difficulty, owing to the various colors made from different materials. Several other methods of removing ink will be given.

(1) Soak in warm water; cover with ammonium hydroxide, and then with orthophosphoric acid. Dry and repeat three or four times, or until the spot is removed.

(2) Soak the spot in a concentrated solution of equal parts of citric acid and alum.

(3) Soak the spot in a solution of oxalic acid, 10 parts; stannic chloride, 2 parts, acetic acid, 5 parts; water to make 500 parts.

(4) Make a powder consisting of equal parts of potassium bitartrate and citric acid. Place the material over a hot plate; pour hot water over it and rub some of the powder into the dampened spot with a spoon.

(5) Red inks, except eosin, may be removed by the use of alcohol and acetic acid; or by chlorine water or Javelle water.

(6) Dilute hydrochloric acid (10%) may be applied, followed by rinsing.

BRIEF BIBLIOGRAPHY

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Owen	Dyeing and Cleaning Textile Fabrics	Wiley
Thorpe	Dictionary of Applied Chemistry	Longmans

CHAPTER XXXIII

FUELS AND ILLUMINANTS

787. Definition. Fuels include everything that may be burned in such a manner as to render the heat evolved capable of being economically applied to domestic or industrial purposes.

788. Kinds of Fuel. Fuels may be divided into

1. Solid fuels, further divided into
 - a. Natural fuels, including wood, where the natural tissues are unaltered, and peat, lignite and coal where the tissues are altered.
 - b. Carbonized fuels, as charcoal and coke.
 - c. Compressed fuels, as briquets, or patent fuel.
2. Liquid fuels, as petroleum, benzine, benzol and alcohol.
3. Gaseous fuels, including
 - a. Natural gas.
 - b. Gas produced by carbonizing solid fuels, as coal gas.
 - c. Gas produced by partially burning solid fuels, as water gas, producer gas and blast furnace gas.
 - d. Gas produced by chemical action, for special purposes, as hydrogen and acetylene.

789. Value of a Fuel. The importance and value of any fuel depends upon its distribution, cost, calorific value and the nature of its combustion.

The Calorific Value depends upon the number of calories of heat liberated when a given weight is burned. There are two units for measuring the calorific value of a fuel. (1) The *Calorie* (large) is the amount of heat required to raise the temperature of one kilogram of water one degree Centigrade, in the neighborhood of 15° C. (2) The *British Thermal Unit* is the amount of heat required to raise the temperature of one pound of water one degree Fahrenheit, in the neighborhood of 60° F. One calorie

is equivalent to 3.9683, or approximately 4, British Thermal Units. The small calorie, $1/1000$ as large as the regular calorie is used in certain cases. Two hundred fifty-two small calories are equal to 1 B. T. U.

The Determination of the Calorific Value of a solid or liquid fuel is accomplished by burning a known weight of the fuel in compressed oxygen in a bomb calorimeter. The number of calories for a gas is determined by burning a measured volume of it at atmospheric pressure in a chamber surrounded by a system of coils through which a flow of water at constant head is maintained. By regulating the flow of the gas and water the gas may be completely burned and the heat transferred to the

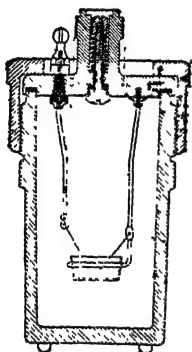


FIG. 175. Iltum Bomb.

water without loss, the products formed leaving the apparatus at a temperature slightly above the atmospheric temperature. Fig. 151 shows a bomb calorimeter. Fig. 175 shows a larger illustration of an illium bomb, with capsule and firing wires.

The gross calorific value is found by taking the sum of all the heat produced in the burning and reducing to the average atmospheric temperature, 15° C. The net calorific value is found by deducting for the heat liberated by the condensation of the steam formed and the constant difference is 11.196 large calories per gram molecule of steam produced.

Some of the values for liquids are (gross) n-hexane, 11620; benzene, 10250; toluene, 10390; methyl alcohol, CH_3OH , 5694; ethyl alcohol, $\text{C}_2\text{H}_5\text{OH}$, 7400. With the alcohols or other homologous series having a constant increase of CH_2 in the complexity, each increase in the complexity gives an increase of 158.5 K. C. gross.

In compound fuels, as coal and petroleum, it is not possible to compute from the analysis the calorific value, since this is never

equal to the sum of the constituents, but for bituminous coal the following formula is approximately correct:

$$Q = 1/100 [8080C + 34,400(H - 1/80) + 2250S]$$

where Q stands for calorific value and C , H , O and S stand for the percentage of carbon, hydrogen, oxygen and sulphur.

The following table shows the gross and net calorific value of some of the common gases in both calories and B. T. U.

	KILOGRAM-CALORIES, (K. C.) (Per gram molecule)		BRITISH THERMAL UNITS B. T. U. (Per cubic foot)	
	<i>Gross</i>	<i>Net</i>	<i>Gross</i>	<i>Net</i>
Hydrogen	68 4	57 2	343 3	287 2
Methane	212 0	189 5	1064 0	951 3
Ethane	370 5	336 9	1860 0	1691 0
Ethylene	333 3	310 9	1673 0	1561 0
Propylene	492 7	459 1	2474 0	2305 0
Acetylene	310 0	298 8	1556 0	1500 0
Carbon monoxide	68 0		341 4	
Cyanogen	259 6		1303 0	

With gases the calorific value is more additive, particularly with water gas and producer gas, where carbon monoxide, hydrogen and methane are the only constituents, but this is not so true when heavy hydrocarbons are present, though it is assumed that these have a calorific value equal to that of propylene, C_3H_6 , and this is not widely different from the real calorific value.

790. Natural Solid Fuels originate in cellulose, $(C_6H_{10}O_5)_n$, which constitutes about 91% of dry wood, with 4% of sap and a small amount of mineral ash, chiefly calcium carbonate and potassium carbonate. Freshly cut wood contains more water than that which has been air dried, the latter containing about 20%, while the former may have up to 40% or more depending upon the kind of wood and the season when it is cut, a smaller percentage being found in wood cut during the winter months. Soft woods have a specific gravity below 0.55, hard woods more than 0.55, and the latter are less inflammable. On account of the

small ash content and its lack of clinkering, wood is well suited for domestic use and for tubular boilers, but is not suitable for high temperatures unless first carbonized (charcoal) or gasified.

791. Peat is widely distributed and more abundant than coal. The amount of peat in the United States is estimated at 14 billion tons, mostly in the eastern states in deposits that average 9 ft. thick. Fresh peat is light brown in color, old peat is dark brown or black with the merest trace of vegetable structure. Peat has a large ash content, 5 to 15%, and the peat beds have a water content of 80 to 90% which is not removed by mechanical means, but by air drying, during the summer season. Air dried peat contains 15 to 25% of water and has a calorific value varying from 2235 to 4300, and averaging about 3000 calories per kilogram, usually considerably less than $\frac{1}{2}$ that of bituminous coal by weight, and about $\frac{1}{8}$ that of coal by volume. The average analysis shows volatile matter 60%, fixed carbon 30%, ash 8%, with 8,500 B. T. U. The combustion is nearly complete. Pulverized peat has been used successfully as a locomotive fuel in Sweden.

While in former years peat was not used extensively as a fuel in the United States, beginning with 1918 it began to be used more and the peat industry assumed great activity and expansion. This development occurred chiefly in the New England States where it was prepared as peat fuel. It is also used as stock food and fertilizer. Black, thoroughly dried, decomposed, friable peat from a deposit that has been well drained and successfully cultivated for several years is usually suitable for an ingredient of commercial fertilizers; or when inoculated with nitrifying bacteria, or when mixed with manure is suitable for a direct fertilizer. The terms peat and muck are often used interchangeably but this is not in accordance with the facts. Peat contains a large proportion of the carbon of the original vegetable matter and in most peat deposits the remains of vegetation are easily visible without a microscope. Peat usually gives an acid reaction and the best peats often contain less than

4% of inorganic impurities. Muck is uncarbonized, organic matter containing a large proportion of inorganic minerals. If the material will ignite and burn freely when dried it is usually considered peat.

The average nitrogen content of raw peat is about 2%. This nitrogen may be recovered in a form of ammonium sulphate or may be made available for plant food without extracting it from the peat. Not all of the nitrogen in peat is soluble at one time, otherwise many, rich, black, peat soils would shortly become unproductive. Since the peat soil is too acid for ordinary farming best results are obtained if they are given over to the production of crops such as buckwheat, oats, corn, rye, potatoes, cranberries, blueberries, strawberries, etc., that can grow in acid soil. If properly treated with potash salts and with lime until they are neutralized or slightly alkaline they will grow other crops such as red clover, timothy, blue grass, wheat, etc.

Peat briquets are usually made from raw peat that has been air dried until the moisture content is 40%. After the peat has been powdered the moisture is further reduced to about 15% by artificial drying. The binder is then mixed with the peat and the mixture is compressed into cylindrical or prismatic shape by means of a piston subjected to a pressure of 18,000 to 31,000 pounds per square inch. But the cost of manufacture is so great that it more than offsets the heating value when compared with the unmolded peat.

792. Lignite, or brown coal, is intermediate between peat and true coal. The lignites are of very little economic importance except in Germany, Austria and Hungary where they are quite widely used. Freshly mined lignite may contain 50% of water which is reduced to 10 to 20% when air dried. Many varieties crumble to a powder when fully dried, but may be pressed into blocks. The ash content varies from 5 to 15% and sometimes higher. Fig. 176 shows a 10 foot vein of lignite.

793. Coal. Several theories concerning the transformation of vegetable matter into coal have been advanced. During the



FIG. 176. Ten Foot Vein of Lignite.

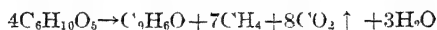
carboniferous age vegetation was abundant. Fig. 177 shows an idealistic view of the vegetation of that period. It is usually



FIG. 177. Vegetation in the Carboniferous Age.

supposed that the earlier stages in the formation of coal were characterized by slow oxidation under water or other covering to protect the decayed wood from direct atmospheric action, and that following this came increased temperature and pressure as more material was deposited over it. If bituminous coal was changed to anthracite it was probably brought about by intense earth pressure accompanied by seismic disturbances, or to the later intrusion of igneous matter from below. There is evidence, at least in some cases, that bituminous coal was formed from the decay of a different kind

of vegetation than that which caused the formation of anthracite. One investigator states that the earlier agencies that helped to transform cellulose into coal were certain fungi and bacterial ferments and represents the transformation for bituminous coal by the following equation



where the formula $\text{C}_9\text{H}_6\text{O}$ shows approximately the composition of many bituminous coals, carbon, 83.1%; hydrogen, 4.6; oxygen, 12.3. It is generally agreed that coal represents only $\frac{1}{5}$ to $\frac{1}{4}$ of the original cellulose and has only $\frac{1}{2}$ its original heating value. In some cases it is thought that the shrinkage in bulk is to $\frac{1}{9}$ of the original volume. Coal is mined to the extent of over 1,000,000,000 tons annually and in 1913 it was estimated that the total amount of coal in the world was 7,397,553,000,000 tons, of which 51.8% was in the United States, which is about 4 times the amount estimated for Germany, and about 20 times that estimated for Great Britain. Fig. 178 shows a comparison of peat, lignite, bituminous and anthracite.

794. Bituminous or "Soft" Coal is classified in various ways according to the purpose to which it is put. The best gas coals are those where the ratio of oxygen to hydrogen is approximately 2, yielding

30 to 38% of volatiles and a fairly porous coke of no great strength. "Coking" coals should contain 20 to 30% of volatiles and are strongly caking. Steam coals should contain less than 20% of volatiles, are non-caking and nearly smokeless. Gas producer coal should be non-caking and have an infusible ash.

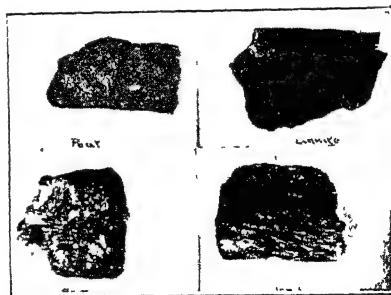


FIG. 178. Comparison of Peat, Lignite, Bituminous and Anthracite.

Nitrogen is present in coal to the extent of 1 to 2% but furnishes 95% of the ammonium salts used, but only about 15 to 17% of the nitrogen in coal is recovered as ammonia, 40 to 60% remaining in the coke, 19 to 37% in the gas, 3 to 4% in the tar and 1 to 1½% as cyano compounds. When coal is distilled the evolution of ammonia begins after caking has set in, at about 350° for bituminous coals and at about 450° for anthracite, the principal evolution being between 500° and 700°.

Sulphur is always a deleterious element in coal and occurs as ferric sulphide, FeS_2 , as sulphates, such as gypsum, CaSO_4 , and as organic sulphur. It is partly expelled as hydrogen sulphide, carbon disulphide and thiophen, but is largely retained in the coke.

795. Coal Ash is usually silicon dioxide, SiO_2 , 25 to 40%; aluminum oxide, Al_2O_3 , 19 to 28%; ferric oxide, Fe_2O_3 , 22 to 32%; calcium oxide, 3 to 16%; magnesium oxide, up to 3.5% and sulphur trioxide, 3 to 8%.

796. When Coal Is Heated to 450° to 500° higher paraffins and methane and very little hydrogen are evolved. At about 700° no more paraffins are evolved, and between 700° and 800° the evolution of hydrogen abruptly and rapidly increases, while methane reaches its maximum at 800° to 900°. It is thought that the paraffins come from the gums and resins and that the hydrogen comes from the decomposition of the cellulose of the plants.

When coal is put into a hot furnace it is partially distilled, the least stable constituents are decomposed and hydrocarbons are evolved, which on partial oxidation or secondary decomposition yield carbon and dense tarry vapors (smoke) difficult to burn, except in an abundant air supply and at high temperatures. The residual semi-carbonized fuel is burned by the air drawn in.

797. The Theoretical Amount of Air necessary for the burning of a given weight of coal is always less than the actual amount required. This is told by obtaining the percentage of carbon dioxide in the chimney gases. The theoretical amount may be

told from the analysis of the coal but the actual amount of carbon dioxide found rarely exceeds 65 to 70% of the theoretical amount that should be evolved, and usually runs 40 to 50%, meaning a large waste, which may be overcome in part by mechanical stoking. Figure 179 shows an automatic stoking furnace such as used at many large establishments. A slow moving grate automatically carries the coal into the combustion zone while the fine ashes drop through the grate and larger pieces are carried to the rear of the furnace and dumped into the ash pit. Automatic instruments for recording the temperature and the carbon dioxide content of the chimney gases are valuable aids towards fuel economy.

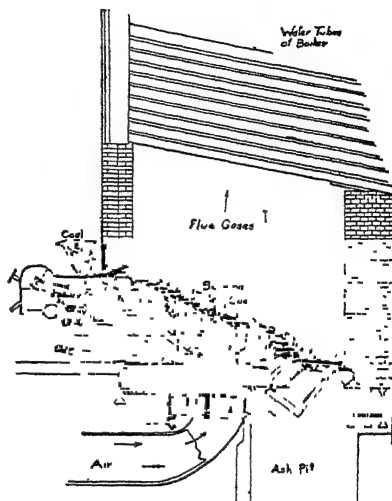


FIG 179. Automatic Stoker for Fuel Economy.

798. For Steam Raising Purposes it has been found that coal containing 16 to 23% of volatiles is the most satisfactory. If the coal contains too high a percentage of volatiles, too much is wasted on account of incomplete combustion, but if the volatiles are too low a large percentage of coke is produced, and an excessive amount of air is required to maintain combustion at the proper rate.

799. Composition of Coal.

Kind of Coal	Carbon	Hydrogen	Oxygen	Nitrogen
Bituminous	75 to 91%	4.5 to 5.5	2 to 18	1 to 2
Anthracite (av.)	91.29	2.91	2.75 (with Nitrogen)	Ash 3.05

In anthracite coal the percentage of nitrogen varies from 0.58 to 2.85 and sulphur is found to the extent of 0.63 to 1.00%. Anthracite is hard and brittle. It has a specific gravity of 1.35 to 1.7 and burns with a smokeless flame.

800. Carbonized Fuels. *Charcoal* was formerly made by igniting wood that was piled in heaps, covered with earth. The gaseous and liquid portions were allowed to run to waste and only the charcoal was considered to have any value. At present the charcoal is only one of the many products that are obtained when wood is distilled in a closed retort. When charcoal is produced at 350° to 400° it is porous, black, sonorous when struck, and has a conchoidal fracture and a ligneous texture. Charcoal burns with no smoke, and when burned in separate pieces produces no flame. Its specific gravity when powdered is from 1.5 to 2 but in the lump form is from 0.2 to 0.35 owing to the large amount of air enclosed in the pores, when made from soft woods, and from 0.35 to 0.5 when made from hard woods.

801. Dry Charcoal is about 90% carbon, 3% hydrogen, and 7% oxygen. After storing it is about 70.45% carbon, 1.68% hydrogen, 13.1% oxygen, 1% ash, 13.76% moisture and gases. The usual ash content is 3 to 4%. The yield of charcoal depends upon the nature, age and condition of the wood and the method used. Where branch wood of fir is used about 31% of charcoal by volume is obtained, while logs of the same give about 80% by volume, if stacked vertically, and somewhat less if stacked horizontally. The weight of the charcoal is from 15 to 28% of the original weight of the wood. Slow charring gives a greater yield of charcoal.

802. Coke is made by carbonizing coal. For metallurgical purposes it should be compact, heavy and homogeneous, with a bright light gray surface. In addition to the carbon, coke contains up to 8% of ash, 0.2 to 1.2% of hydrogen; from traces up to 8% of oxygen; 0.4 to 1.5% of nitrogen; and from 0.8 to 1.8% of organic sulphur. The best cokes are 90% carbon, and less than 8% ash, and have a metallic ring. Coke, when dried, does

not absorb more than 1 or 2% of moisture, and when on the market should not contain more than 3%. Coke having 90% carbon and 0.5% hydrogen has a calorific value of about 7,450 large calories per kilogram.

803. Compressed Fuels. *Briquets* are made by compressing into blocks, weighing 10 to 30 pounds each, fine anthracite, semi-anthracite, semi-bituminous slack, bituminous slack, anthracite culm, sub-bituminous coal, and oil gas residue. The binders used include coal tar pitch, asphaltic pitch, sulphide pitch, etc.

The production of fuel briquets increased from about 70,000 tons in 1907 to more than 477,000 tons in 1918. Briquets often stand transportation better than the original coal and as a steam raising fuel is frequently more satisfactory.

804. The Value of a Coal depends upon its calorific value and upon special features determined by the purpose for which it is to be used such as (1) the moisture content; (2) the quantity and fusibility of the ash; (3) the percentage of volatiles; (4) the ultimate analysis showing the percentage of carbon, hydrogen, oxygen and nitrogen, the latter being important if the coal is to be carbonized or gasified in producers under ammonia recovery conditions.

805. Spontaneous Combustion of Coal is due to the condensation of oxygen in the pores of the fuel; oxidation of certain constituents of the coal substance and possibly to bacterial action. At 150° to 200° coal readily absorbs oxygen, oxidizing the coal substance. The weight at first increases owing to oxidation, but then decreases, owing to loss of moisture, slow combustion and decomposition. At temperatures between 200° and 275°, depending upon the nature of the coal, its fineness, etc., oxidation becomes autogenous, but actual ignition does not occur until a temperature of 350° is reached. Coal should, therefore, be stored where there is an excessive ventilation or where there is none at all.

806. Liquid Fuels are used to a limited extent for certain selected purposes, and have some advantages over solid fuels,

since a given weight requires less space for storage and they have a greater steam raising power than coal, in the ratio of 3 to 2.

807. **Crude Petroleum**, found in Pennsylvania, Ohio, Illinois, Virginia, Louisiana, California, Wyoming, Texas, Oklahoma, Kansas, Russia, Galicia, Roumania, India and the Eastern Archipelago is pumped from the earth to the extent of

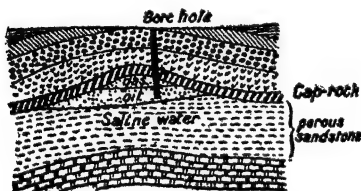


FIG 180 Drilling for Oil.

about 3,000,000,000 gallons annually, 62% coming from the United States. Fig. 180 shows a boring through different strata to reach an oil deposit. Some water in emulsified form, and volatile hydrocarbons occur with petroleum and must be

removed before it can be shipped, stored or used safely. Fig. 181 shows a general view of an oil field; Fig. 182 shows oil flowing from a well; and Fig. 183 shows a burning oil well.

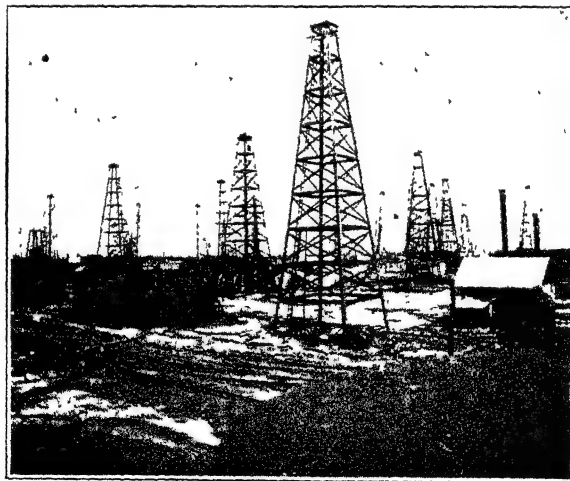


FIG. 181. View of an Oil Field in Louisiana.

Petroleum consists essentially of hydrocarbons but contains small and varying amounts of nitrogen, sulphur and oxygen,



FIG. 182. Oil Flowing from a Well.

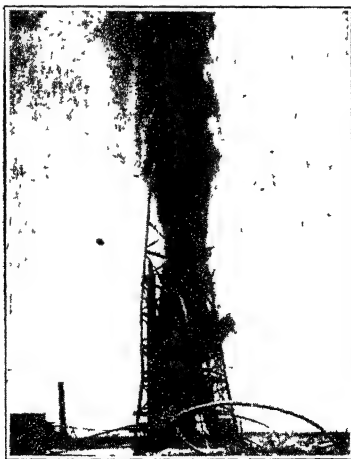


FIG. 183 Burning Oil Well

which occur as various compounds in oils from different countries. The hydrocarbons are chiefly paraffins, C_nH_{2n+2} , naphthalenes,

C_nH_{2n} , and members of the groups varying from C_nH_{2n-2} to C_nH_{2n-12} . While hydrocarbons such as naphthalene, acenaphthalene, fluorene, anthracene, and phenanthrene are found in coal tar, only naphthalene is found in petroleum. The gross calorific value of crude petroleum is between 10,350 and 11,000 large calories per kilogram. In using oil as a fuel it must first be atomized by a jet of high pressure steam or by compressed air. The oil should enter the furnace as a fine spray, intimately mixed with the air necessary for its combustion. In order to secure complete combustion and to prevent the formation of smoke the flame should not come into direct contact with cold metallic surfaces. Petroleum oils are also used to an enormous extent in internal combustion engines, gasoline being used the most, while kerosene and crude oils of higher boiling points are used in limited amounts.

808. Refining of Petroleum. The oil is subjected to fractional distillation, the distillate being usually divided into

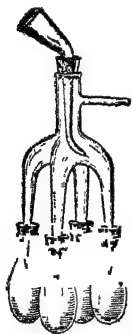


FIG 184. Receiver for Fractional Distillation in the Laboratory.

naphthas, illuminating oils, lubricating oils, paraffins and coke. The distillation usually falls into two stages—the distillation of light oils and heavy oils. The light oils are distilled from a cylindrical or large circular still, holding from 600 to 1,000 barrels. Condensation occurs in straight pipes immersed in cold water. Fig. 184 shows a small laboratory type of receiver for fractional distillation. The bent movable tube at the top is turned to permit the distillate to flow into any one of the flasks. The commercial products of petroleum, their uses and the temperatures at which they are obtained are as follows:

Cymogene and rhigolene, used sometimes in artificial ice machines, pass over at temperatures lower than 70° F. Ligroin or petroleum ether, a purified, low boiling product, used as a

solvent in laboratories, is collected at a temperature of about 70°. Low boiling gasoline passes over between 70° and 90° and is so volatile that air saturated with its vapor may be burned as illuminating gas. High boiling gasoline passes over between 90° and 150° and is used in gasoline stoves. It is nearly or quite identical with naphtha and benzine which are used for cleaning. Kerosene as used in lamps is collected between 150° and 300°. Lubricating oils distil between 300° and 400°. Paraffin passes over at temperatures above 400° and coke is left in the retort. Any distillate may be redistilled for purification.

809. Increasing the Yield of Gasoline. When 10% of aluminum chloride is added to kerosene, lubricating oil or paraffin and slowly heated, the salt dissolves, making the liquid dark brown. When the brown liquid is distilled the portion passing over between 40° and 140° is the same as petroleum benzine, and is about 35% to 50% of the kerosene. By heating to 400° other products are obtained, and finally a black viscous residue remains, from which the aluminum chloride is removed by lixiviation, while the black substance is similar to asphalt. The total gasoline obtained is from 11% to 56% of the original material, and has somewhat greater heating power than natural benzine. The composition of this gasoline is about 35% of the series C_nH_{2n+2} , chiefly C_6H_{14} and C_7H_{16} , and about 65% of the series C_nH_{2n} , chiefly C_7H_{14} and C_8H_{16} .

Gasoline may also be obtained from natural gas by compression and cooling, and the partially denuded gas is subjected to absorption processes. The products derived are blended and the vapor tension is reduced by driving off the more volatile portions to obtain the finished product. During the 8 years from 1911 to 1918, 755,497,000 gallons of gasoline were produced from natural gas. The natural gas is improved by the process owing to the removal of water.

Since petroleum is a mixture of many hydrocarbons of the marsh gas and ethylene series, and the average formula for gasoline approaches C_6H_{14} , many higher members of these series

are present in the natural petroleum. When this is subjected to distillation under pressure some of the higher members break up into two or more of the lower members of the series, and in that way the yield of gasoline is increased. This is usually called "cracking" the heavy hydrocarbons.

It is estimated by the United States Geological Survey that the petroleum deposits will be exhausted by 1935.

810. The Flashing Point as Determined by Law varies from 44°C. to 65.5°C. (111° to 150°F.) and may be determined for a given sample as follows:

Oil is poured into the cylinder, *a*, (Fig. 185) which is fitted with a wooden plug and tube terminating in a small opening. The oil is slowly heated on a water-bath and compressed air is slowly forced through the oil at such a speed that foam five centimeters thick is formed. The temperature is taken by means of a thermometer and a lighted match is held at the mouth of the cylinder every time the temperature rises one degree. When the oil has become heated to the flashing point the vapor will catch fire and the flame will pass down to the surface of the oil. Fig. 186 shows Abel's apparatus for determining flash point. This type of apparatus is standard in Germany and Great Britain.

811. Solidified Liquid Fuel or Solid Alcohol is made according to a patented process from pyroxylin, 1 ounce; ether, 36 ounces; and alcohol, 12 ounces; dissolved together, then mixed with additional alcohol; heated, partially to drive off the ether, and then cooled. The resulting mass is slowly, but completely combustible.

812. Gaseous Fuels. *Natural Gas* occurs usually in petroleum districts issuing from a depth of 500 to 2,000 feet, with a pressure of 250 to 400 pounds per square inch. It is used industrially to an enormous extent where it is available. Its composition varies, but is chiefly methane, 64 to 94%; hydrogen, 3 to 30% with small amounts of ethane, ethylene, carbon monoxide

and nitrogen. The density of the gas (air = 1) is from 0.45 to 0.55.

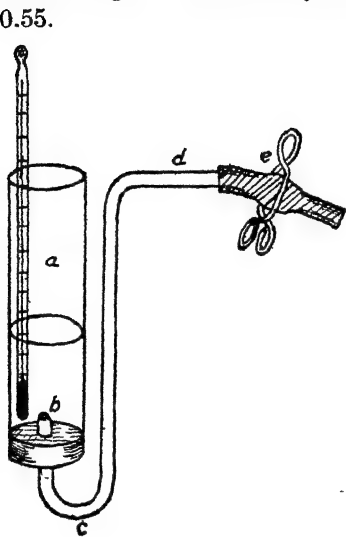


FIG. 185. Simple Apparatus for Determining the Flash Point of Oil.

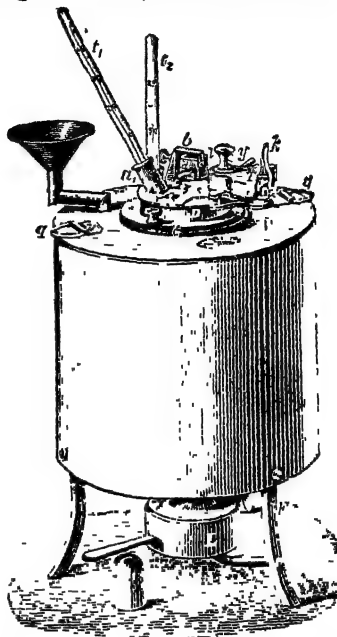


FIG. 186. Abel's Flash Point Apparatus.

813. Coal Gas is obtained from the distillation of bituminous coal in retorts, and is freed from tar, ammonia and hydrogen sulphide (Fig. 187). The composition of the gas depends upon the coal, the nature of the retorts and the temperature employed. Good gas contains from 45 to 50% hydrogen; 30 to 35% methane; 4% heavy hydrocarbons, reckoned as C_3H_8 ; 5 to 10% carbon monoxide with not more than 5% nitrogen. Its calorific value should be not less than 575 net and 645 gross B. T. U. per cubic foot at 0° and 760 mm. pressure. It is very economical for domestic purposes and has many advantages over raw wood or coal.

From a ton of bituminous coal may be obtained from 9,000 to 11,000 cubic feet of gas, 1,500 pounds of coke, 20 gallons of ammonium hydroxide, and 140 pounds of coal tar. From the

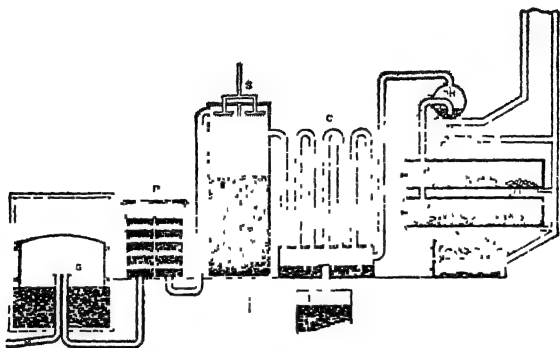


FIG. 187 The Manufacture of Coal Gas.

distillation of the coal tar may be obtained 69 pounds of pitch, 17 pounds of creosote, 14 pounds of heavy oils, 9 pounds of

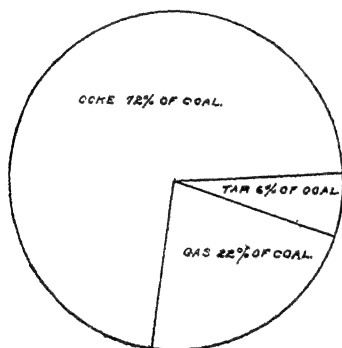


FIG. 188. Percentage of Coke, Gas, and Tar from Coal.

naphtha yellow, 6 pounds of naphthalene, 4 pounds of naphthol, 2 pounds of alizarin, 2 pounds of solvent naphtha, and about a pound of each of aurine, benzene, aniline, toluidine and toluene. By proper treatment these substances yield an enormous number of other substances, used for dyeing; and others, such as saccharin, which is about 500 times as sweet as sugar. See Fig. 188.

The Republic by-product coke plant at Youngstown, Ohio, is equipped with 143 Koppers 13.25 ton ovens built for the complete recovery of all by-products. The plant has a daily capacity

of 2,800 tons of coal, and produces 1,900 tons of furnace coke, 140 tons of breeze coke, 61,000 pounds of ammonium sulphate, 25,200 gallons of tar, 16,000,000 cubic feet of gas, and 8,000 gallons of benzene. Fig. 189 shows a general outline of the distillation of coal.

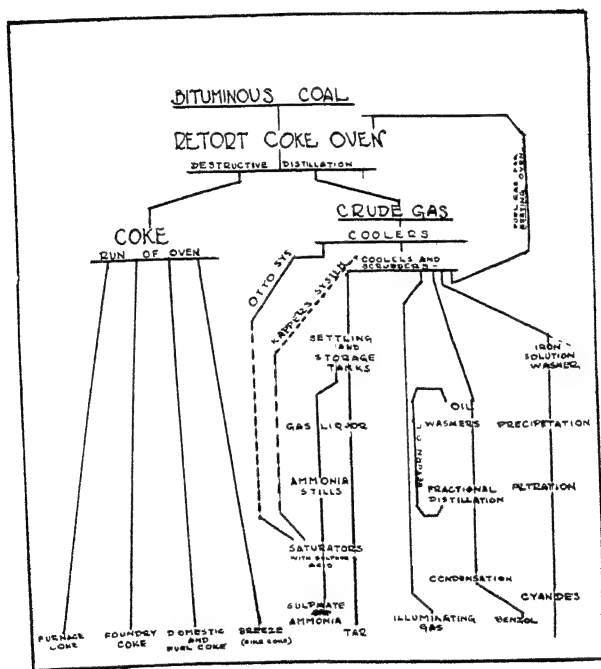


FIG 189 Outline of the Distillation of Coal

The new gas plant at Chicago has 100 Koppers ovens, and 9 water gas sets, with by-product recovery plant. The gas output is 14,000,000 cubic feet of coke oven gas and 25,000,000 cubic feet of water gas daily.

It is claimed that with the Dempster-Toogood vertical retorts each ton of coal will yield 22,000 cubic feet of gas and 1,450 pounds of coke.

(See Fig. 191), whereby the solid fuel is converted into gas containing 35 to 45% of combustibles—carbon monoxide, hydrogen and methane. The fuel is dropped into the producer through a bell hopper on the top and undergoes distillation as in retort distillation, evolving hydrogen and methane, tarry hydrocarbons, carbon monoxide, and small quantities of ammonia, hydrogen sulphide, etc. Olefines and higher paraffins are so rapidly decomposed that they do not appear in the gas passing out of the producer. The coke is gasified in the lower part of the fuel bed by interaction with the ascending air-steam blast, yielding the mixture of substances mentioned above. When dry

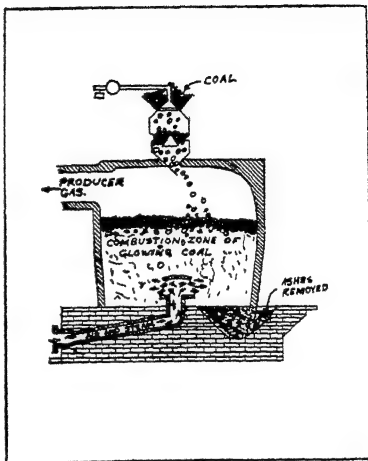
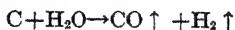


FIG 191. The Manufacture of Producer Gas.

air alone is used, the reaction between the air and the coal is shown by the equation $C + O \rightarrow CO$ and this may be replaced by the reversible reaction shown by the equation $2 CO \rightleftharpoons C + CO_2$. The relative proportion of the carbon monoxide and carbon dioxide depends upon the temperature, less carbon dioxide being evolved at high (1,200° to 1,400°) than at lower temperatures, and with good coke it is possible to produce a gas containing 0.5% carbon dioxide; 33% carbon monoxide; 1.5% hydrogen and 65% nitrogen. Steam acts upon the carbon in two ways the reaction at 500° to 600° being shown by the equation



which gradually changes into



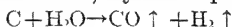
as the temperature rises, the latter occurring exclusively at 1,000°, or more.

815. For Furnace Purposes it is best to have the carbon monoxide content as high as possible and not more than 12 to 14% hydrogen. For some uses the gas must be purified by passing it through a water spray to remove the dust and tarry vapors; through a solution of ammonium sulphate containing about 5% free acid to remove the ammonia, the solution flowing in a direction opposite to that of the gas; then over dry coke to remove the sulphate liquor. From coal containing 1.2 to 1.25% nitrogen it is possible to recover 90 to 100 pounds of ammonium sulphate per ton, and to produce 140,000 cubic feet of gas containing 16.5 to 17% carbon dioxide; 10.5 to 11% carbon monoxide; 26.5 to 27% hydrogen and 2.6 to 2.8% methane.

816. Blast Furnace Gas, produced in smelting iron ore, is generated at the rate of 168,000 cubic feet per ton of ore when coke is used as fuel. It is approximately 12% carbon dioxide; 30% carbon monoxide, (including 0.5 to 1.0% hydrogen); and 58% nitrogen, and has a calorific value of 24 to 25 large calories per cubic foot. From a furnace producing 1,000 tons of pig iron per week this means 1,000,000 cubic feet of gas per hour, the potential energy of which is about 45% of the energy of the coke used, and is sufficient to supply the heat necessary to operate blowing engines, gas engines for operating dynamos, heating the stoves that supply the blast, etc. The gas leaving the top of the furnace has a temperature of about 300° and is heavily charged with dust. The latter is removed by (1) dry cleaning with any dust catcher, reducing the dust to 2 to 8 grams per cubic meter; (2) preliminary washing by passing the gas through a cylindrical steel chamber in which revolves a horizontal shaft, carrying a series of circular discs of thick wire with a coarse mesh, the lower half of which is submerged in water, and the gas is partly cleaned by passing through the water films, reducing the dust to 0.5 gram per cubic meter; and (3) final washing by a centrifugal apparatus, in which the gas is

violently churned with a fine spray or stream of water. Sometimes only the first and third methods are used, but the dust must, in any case, be reduced to about 0.01 gram per cubic meter before it can be used in engines.

817. Water Gas is made by blowing air through a bed of incandescent coke until a high temperature is reached, followed by blowing steam through the incandescent mass as long as carbon monoxide is formed, by the equation



without the formation of carbon dioxide

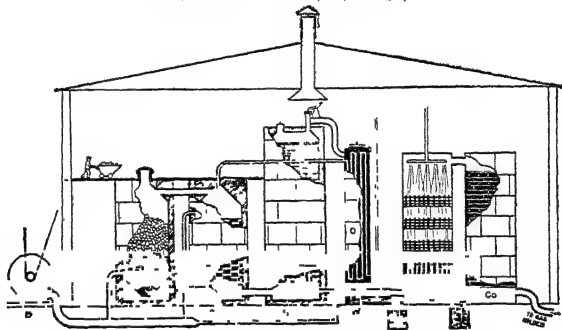
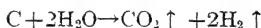


FIG. 192 The Manufacture of Water Gas.

When the latter reaction begins the steam and gas valves are closed and the air and stack valves are opened. Air is again blown in until the temperature is high enough to bring about the first reaction. Usually the air is blown in for about one minute and the steam for about four minutes. With average coke 32 cubic feet of gas can be produced per pound of coke used or 64,000 cubic feet per ton. The average composition is theoretically 50% each of carbon monoxide and hydrogen, but the actual average composition is 4% carbon dioxide; 43% carbon monoxide; 49% hydrogen; 0.5% methane; and 3.5% nitrogen with a net calorific value of about 75 large calories per cubic foot.

For Illumination water gas is very poor unless it is enriched by the addition of hydrocarbons—ethane, ethylene, acetylene and benzene—ethylene and benzene being the most important. Carbureting is brought about by passing the gases from the generator to the carburetor where they come in contact with a stream of oil, which is decomposed by passing over hot “checker work” of fire bricks with which the carburetor is filled.

818. The following table shows a brief comparison of the different kinds of gas used for heating:

Kind of gas	Net calories per cu. ft.	Volumes of air to burn one volume of gas	Vols. of gas and air in cu. ft. required for 25 calories or 100 B. T. U.	Volume of products including water per 25 calories or 100 B. T. U.
Blast furnace	25	0 715	1 715	1 565
Producer	37 5	1 216	1 480	1 357
Water	72 5	2 200	1 100	0 953
Coal	147 5	5 440	1 100	1 050



Fig. 193. A Pyrometer for Measuring High Temperatures.

819. High Temperatures are measured by pyrometers or by Segar cones. In the radiation pyrometer, (shown in Fig. 193) the rays of heat from the furnaces or molten substance, enter the pyrometer tube, are reflected from a concave mirror to a sensitive thermocouple, the temperature being indicated by a milli-volt meter, graduated in temperature degrees. The Segar cones (Fig. 194) measure temperatures from 600° C. to 2,000° C. Cones having different numbers for

identification melt at different temperatures, the melting points for consecutive cones differing by 20 to 50°.

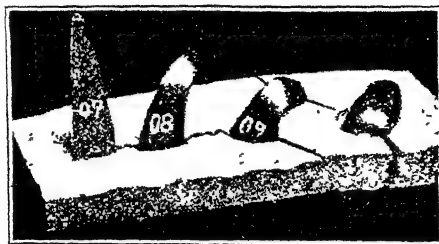


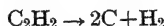
FIG 194. Segar Cones, Melting at Different Temperatures.

The highest temperatures obtainable with different fuels have been stated to be

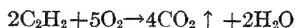
<i>Fuel</i>	<i>Temp. C.</i>	<i>Temp. F</i>
Bunsen burner with plenty of air	1871	3400
“ “ “ not enough air	1712	3114
Alcohol	1705	3101
Acetylene	2548	4618
Hydrogen free in air	1900	3452
Oxy-coal gas with blow pipe	2200	3992
Oxy-hydrogen “ “ “	2420	4388
Oxy-acetylene “ “ “	3000—4000	5432—7232
Electric arc	3760	6800
Sun	7800—10000	14075—18000

Only under the best conditions can these temperatures be obtained, so that they are usually less than the ones given in the table.

The reason for the high temperature of the oxyacetylene flame is that we have the positive heat of decomposition added to the heat of the oxidation of the carbon and the hydrogen. When a gram molecule of acetylene decomposes



58,100 calories (small) are evolved, and when it burns with oxygen



the heat of combustion is 4×96480 for the carbon, and 4×28800 for the hydrogen, so that the total is more than can possibly be obtained from the oxyhydrogen flame. With the oxyacetylene flame steel 6 inches thick may be melted in less than one minute.

820. Gas Mantles originated from the discovery that a piece of dense lime held in an oxyhydrogen flame gave rise to intense incandescence. This is known, as the oxyhydrogen, calcium, lime or Drummond light, but it was not until 1883 that Welsbach discovered that oxides of rare metals emitted intense light when heated to incandescence.

In 1886 Welsbach patented the use of thorium oxide either alone or combined. Thorium oxide alone does not emit much light and the light he obtained was due to cerium oxide present as an impurity, so that later patents covered the use of thorium oxide with one or two per cent of oxides of rare metals including cerium, so that the commercial mantles are now 99% thorium oxide and 1% cerium oxide. Thorium nitrate is converted into the oxide by heating, and swells to ten times the original volume, containing minute air cells. If more than 1% of cerium oxide is used the intensity of the light decreases, until when it is present to the extent of 10% no light is emitted. Cerium nitrate does not expand when heated to the oxide, so that although present as 1% by weight, it is only 0.1% by volume. (Fig. 195.)

The original mantles were made of cotton. They were knitted, cut into lengths, folded over and fastened with an asbestos loop, then dipped into a solution of the two nitrates. They were then passed through rollers to squeeze out the excess of the solution, leaving enough to form 0.5 to 0.7 gram on the finished mantle. The cotton was then burned out leaving a skeleton of the oxides. It was then dipped into a solution of collodion, 20 parts; ether, 18.3 parts, castor oil, 0.96 part; and camphor,

1.5 parts, the last two to prevent over-contraction in drying. They were then dried, trimmed and packed.

When ramie fiber is freed from its glutinous coating it can be woven into a silk-like material and made into mantles similar to the collodion fiber, so that it has practically displaced cotton.

In using a mantle the ratio of air to gas should not be less than 2.2 to 1 otherwise some methane escapes combustion in the inner zone of the flame and burns with carbon monoxide and hydrogen in the outer zone producing a sooty deposit of carbon which rapidly destroys the mantle.

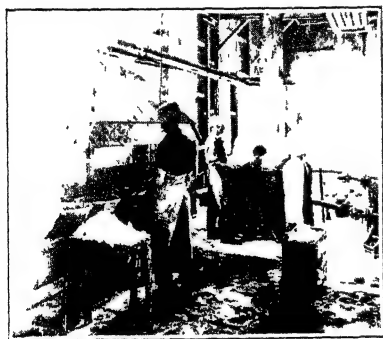


FIG. 195 The Manufacture of Gas Mantles

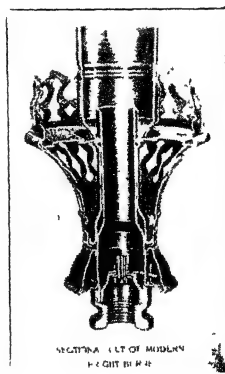


FIG. 196 The Upright Burner

The mantles are used with special burners. Fig. 196 shows the section of an upright burner; Fig. 197 shows the section of an inverted burner; and Fig. 198 shows a modern reflex lamp complete.

One explanation of the action of the thorium and cerium oxides is that thorium oxide is a good non-conductor, has a low specific heat and low radiating power and can, therefore, be raised to the flame temperature. Cerium oxide has great radiating power and cannot be raised to the temperature neces-

sary to give light. When mixed, the cerium oxide particles are so insulated by the large excess of thorium oxide (1 to 1,000 by volume) that it is brought to the temperature of the flame and its catalytic action upon an air and gas mixture seems to focus the combustion of the extremely attenuated flame gases upon the widely separated cerium oxide particles and therefore raises them to a far higher temperature than the mantle. The addition of more cerium oxide produces a rapid cooling, so that by

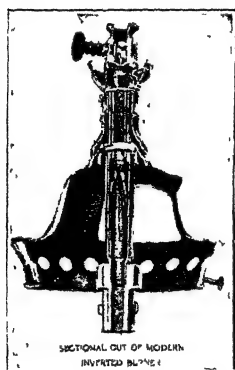


FIG 197. The Inverted Burner.

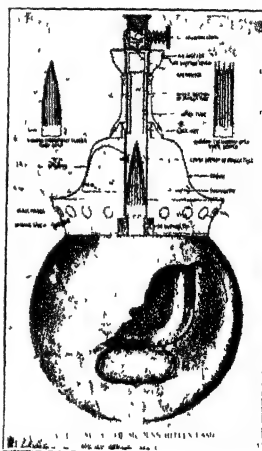


FIG. 198. The Modern Reflex Lamp.

the time 10% is reached no more light is given than from a mantle made of thorium oxide alone, but there is a greatly increased heat radiation.

821. Pintsch Gas, used in railway coaches, is made in a manner similar to the manufacture of coal gas, with the exception that naphtha is used instead of bituminous coal as the source of the gas. After purification the gas is dried by being pumped through a cylinder which causes expansion and therefore loss of moisture. It is then forced into large tanks from which it is

drawn into smaller tanks or storage cylinders. The gas gives an intense white light and loses but little illuminating power by being compressed for shipment.

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Smith	Coke Oven and By-products Works Chemistry	Lippincott
Tindlar and Challenger	Chemistry of Petroleum	Crosby, Lockwood & Son
Wagner	Coal Gas Residuals	McGraw-Hill
Warnes	Coal Tar	Pitman
Young	Fractional Distillation	Macmillan

CHAPTER XXXIV

PAINTS, OILS AND VARNISHES

822. Paint Consists essentially of an oil containing a metallic salt in suspension, of such a consistency that it may be easily spread with a brush, and should dry with moderate rapidity, which may be hastened by the use of a drier, but the drying should not be so rapid as to cause cracking. It may be said that the paint contains a vehicle, a pigment and a drier.

Paints are Distinguished from Dyes by the fact that in painting only the surface is covered, while a dye stains the material throughout.

823. Oils are Classified according to their source as animal, vegetable and mineral; for use they are classified as non-drying, semi-drying and drying.

Non-drying Oils are those like olive, sperm, whale, cocoanut, lard, etc., which on exposure do not change, or at least become only slightly thicker. They are not good for paints but are used for the lubrication of machinery.

Semi-drying Oils include a few of the common oils like cottonseed and corn. On exposure they become more viscous and gummy, but never dry hard. They are good for neither painting nor machinery, but may be used as foods, in the manufacture of soap, etc.

Drying Oils such as linseed, poppy seed, Chinese wood or tung, hempseed and walnut will, when exposed to the air, especially in thin coats, absorb oxygen and form a hard firm mass, good for paints but not good for machinery.

824. Oils may be Considered as glycerides of fatty acids. Most oils contain two or more acid radicals. On saponification with an alkali glycerin and a soap are formed. The acids present, to a greater or less extent in all oils, are oleic,

stearic, and palmitic, while others are found only in special oils, of which they form the characteristic constituent, as linolic in linseed oil, ricinoleic in castor oil, etc. Oleic is by far the commonest of all fat acids and when combined with glyceryl it forms olein, the fluid constituent of almost all oils, as well as pork fat.

Linolic and Linoleic acids are characteristic of linseed and other drying oils, and form soaps like the acids of the stearic and oleic series of acids, but more soluble in water.

825. Drying Oils are comparatively few, and of these the best is linseed. Chinese wood oil or tung oil is used to some extent; poppyseed and walnut oils are used by artists on account of the light color, but are too expensive for ordinary use. Hempseed is used in Russia, and Menhaden fish oil is used to some extent in the United States. Other drying oils are of little interest.

826. Linseed Oil is derived from flax seed which is first cleaned to free it from dirt and other seeds. The seed is then crushed, heated and pressed, first with a pressure of 750 pounds per square inch, and then with a pressure of two tons, giving a yield of oil equal to about 30% of the weight of the seeds. The crude oil contains the glycerides of the linseed oil acids, water, mucilage, albumen, etc., coloring matters of the chlorophyll group, giving varying shades of green and brown to the oil. The oil is then refined to rid it of the water, mucilage, albumen, etc., and may be left in large tanks, warmed to 100° to 110° for 3 to 6 months, when the impurities settle out as a sediment, called "foots" and the clear transparent oil, possibly highly colored, is on top. The method is slow and not often used, but it gives the best oil for varnish making.

A More Rapid Process is to warm the oil with a steam coil to 150° to coagulate the albumen, filter it through a filter press and treat it with 3 pounds of sulphuric acid for every 112 pounds of the oil, the acid being diluted with an equal volume of water. This takes out the albumen and coloring matter. Air is blown

through to mix the oil and acid, and after standing the acid settles to the bottom and is drawn off. Clean warm water is added to remove the last traces of the acid.

827. Raw Linseed Oil is oil made as above. It has a characteristic odor and taste. Its specific gravity varies from 0.932 to 0.937 with an average of 0.935 at 60° F. Linseed oil when exposed to the air gradually absorbs a large proportion of oxygen forming a new compound of resinous character that has not been fully studied.

828. Boiled Oil has greater drying powers than the raw oil. It is of three kinds, (1) fire boiled; (2) steam boiled; and (3) so-called cold boiled.

In fire boiling the oil is placed in large iron pans and the heat is gradually and carefully applied until a temperature of about 500° F. is reached. It is boiled for a half hour and small quantities of driers are added from time to time for a period of three hours. Driers will be more fully described in §835. The average amount required in fire boiling is about 5 pounds of drier per ton of oil. After boiling for another hour the oil is allowed to cool over night. The clear oil at the top is sold for the manufacture of paint, and the lower part, known as "boiled oil foots" is used for putty or in cheap ready mixed paints. During the boiling, water and irritating vapors of acrolein, formic acid and acetic acid are given off. The amount of color in the boiled oil increases with the temperature and depends to some extent also upon the nature of the drier used, manganese dioxide giving the darkest oil, while lead monoxide (litharge) and lead tetroxide (red lead) give an oil not as dark as the manganese, but darker than the other driers that are used.

In steam boiling a double cased iron pan is used and steam is admitted between the walls. The oil is heated for about two hours to about 210° F., and is stirred well. Then the driers are added gradually. The heating is continued and air is forced through the oil for 6 to 8 hours. From $\frac{1}{2}$ to 1 pound of drier is required for each 100 pounds of oil boiled by this method. The

oil is lighter in color and gives a more elastic coat than the fire boiled oil. There are several modifications of these methods.

The third method has several modifications but one will illustrate. The raw linseed oil is mixed with a solution of manganese linoleate in turpentine, and the oil is then sprayed into a room filled with ozonized air, the spraying being repeated several times. A quick drying oil is obtained, which is paler in color than the raw oil and dries with a more elastic coat than the ordinary boiled oil.

829. Properties of Boiled Oil. Boiled oil is usually a slightly viscous liquid of a reddish color. It has a peculiar odor. The specific gravity varies from about 0.940 to 0.950, averaging about 0.945. Boiled oil dissolves in turpentine, petroleum spirit, shale spirit, benzene, carbon disulphide, and other similar solvents. It may be saponified completely when boiled with either sodium hydroxide or potassium hydroxide. Boiled oil is rapidly oxidized when exposed to the air in thin layers, but it is usually mixed with a little raw oil so as to make the coat more elastic.

830. Adulteration of Linseed Oil is common, the chief adulterants being mineral and rosin oils. The great difference in the cost of mineral oil and linseed oil make the former one of the most commonly used adulterants. If the specific gravity of the raw oil is less than 0.930, it is probably adulterated with mineral oil; while if it exceeds 0.937, it is probably mixed with rosin oil. The flash point of linseed oil is about 500° F. Rosin oil flashes at 300° to 330° and mineral oil at 380° to 420°. The detection of other fatty oils is much more difficult.

Boiled Oil Substitutes, some of which are patented, are offered. They may consist of mixtures of boiled oil, rosin, turpentine, and rosin oil, or are more like a varnish, being made by melting rosin, mixing it with hot oil and thinning with turpentine.

Other Drying Oils are not used in house painting in the United States, in large quantity. Most of them are too expensive, and

are used for painting pictures, where the cost of the material does not enter so largely into account.

831. Thinners, or Solvents, are liquids such as turpentine, coal-tar naphtha, petroleum spirit, benzene, methylated spirit, etc., having a comparatively low boiling point, and easily distilled.

832. Turpentine, also called spirit of turpentine, oil of turpentine, or by painters, "turps," is derived from various species of pine trees. American turpentine is obtained from the Georgia pine, found largely in North and South Carolina, Georgia and Florida. During the winter the trees are boxed—that is, a cavity is cut into the side of the tree about a foot from the ground, the boxes having a capacity of two or three pints. (Fig. 199.) Resin



FIG. 199. Boxing Trees for Turpentine

flows from the cut surface, and the crude resin is distilled in a steam still heated by fire, the steam being passed through a steam pipe. The turpentine passes over through the condenser and the residue is rosin. The turpentine is often purified by a second distillation. If a sample of turpentine is distilled in the laboratory it will be found to boil at about 150° to 160° and if the sample is of a high grade it will all pass over before the temperature has reached 170° . In low grades a small amount of rosin is left in the retort.

833. Properties of Turpentine. Commercial American turpentine is a water white, limpid liquid with a peculiar and characteristic odor that distinguishes it from all other bodies. The

specific gravity varies from 0.864 to 0.873, averaging about 0.867. Turpentine burns readily with a smoky flame. Its flash point is 36° to 38°. It mixes with ether, carbon disulphide, alcohol, benzene, petroleum spirit, but not with water. It is a good solvent for oils, fats and resins. Turpentine absorbs oxygen slowly from the air causing it to become thick, and prolonged exposure will cause it to become resinous, while a part of the turpentine volatilizes. In painting, the turpentine is spread out in a very thin layer and there is a higher percentage of volatilization, with a more complete oxidation of the residue. This resinous residue acts as a binding agent to fasten the pigment to the surface of the wood.

834. Substitutes and Adulterations. Many substitutes for turpentine may be obtained, consisting largely of the substances used to adulterate the genuine article. These substances are petroleum spirit, shale naphtha, rosin spirit, and coal-tar naphtha. Usually the fact that the turpentine is adulterated, and the nature of the adulteration may be easily detected, but the amount of the adulteration is not so easy to determine. Changes in the specific gravity and in the temperature of distillation are indications of adulteration. A lowering of the two would indicate petroleum spirit and shale naphtha, while an increase in the distillation temperature covering a wide range, and an increase of the specific gravity would indicate rosin spirit.

Rosin Spirit is the best substitute for turpentine known. The rosin is distilled in superheated steam, and a limpid, water white to straw colored liquid is obtained, having a peculiar and characteristic terpene odor. Its specific gravity varies from 0.876 to 0.883 but it is always heavier than turpentine. Exposed to the air it acts the same as turpentine but not to the same extent. If the rosin spirit is not carefully prepared it will contain traces of rosin oil which will prevent its drying properly.

Shale Spirit or shale naphtha, is obtained from the distillation of shale. The first product is redistilled and this is further

purified by treatment with sulphuric acid to remove the basic impurities and then with sodium hydroxide to remove the acid impurities, and is then redistilled. Three products are obtained, one of them being green naphtha, which is treated with sulphuric acid and sodium hydroxide and redistilled, yielding shale naphtha, a water white, very limpid liquid, the yield being about 5% of the crude oil. Its specific gravity varies from 0.730 to 0.760. It is highly inflammable, and very volatile and evaporates without leaving any residue. It is a good solvent for many of the oils and gums, especially when the latter have been partially decomposed by fusion. It is a fairly good substitute for turpentine.

Petroleum Spirit, commonly known as benzine, (not benzene), is obtained from the distillation and refining of the products obtained from petroleum. The distillation products of petroleum are more fully described beginning with §808.

Coal-tar Naphtha is one of the many products obtained from the distillation of coal tar. It is not used to any extent in paints, except as an adulterant or substitute, but is used in varnish making. It is a water white liquid whose specific gravity varies from about 0.865 to 0.877. When distilled, from 8 to 30% passes over at a temperature below 130°, and usually 90% passes below 160°.

Methylated Spirit is a mixture of 90% ethyl alcohol with 10% of methyl alcohol. Both of these compounds are fully described beginning in §695. It is used largely in making spirit varnishes. Ethyl alcohol is frequently called spirit of wine. The alcohol frequently met with in commerce is called rectified spirit of wine and contains 86% of real alcohol. "Proof Spirit" contains 49% of alcohol, but is a term that should be discontinued.

835. Driers. Many paints containing lead and chromium dry much faster than those containing barium, lampblack, ultramarine, etc. It was also found that paints to which certain

compounds of lead, manganese, etc. were added dried much faster than those where these substances were not used.

The Rapidity of Drying with any drier depends largely upon the amount of drier used. Driers that will dissolve readily in the oil are more active than those that do not. Among the more commonly used driers are

Lead Linoleate, made by preparing a neutral soap from linseed oil and sodium hydroxide, and pouring this into a solution of lead acetate. It dissolves quite easily in hot linseed oil.

Manganese Linoleate is made by adding a solution of soap made from linseed oil to a solution of manganese sulphate. It dissolves freely in hot linseed oil and is a most effective drier.

Manganese Resinate is made by pouring a solution of rosin soap into a solution of manganese sulphate. The rosin soap is made from rosin and sodium hydroxide. In drying properties the manganese resinate resembles the linoleate.

Lead Resinate is made by adding rosin soap to a solution of lead acetate, or by melting rosin and lead acetate together. It is fairly effective.

Among the Other Driers are many of the lead compounds such as lead acetate, the oxides of lead, ferrous sulphate, etc., which may be used singly or combined with other driers. A liquid drier may be made by boiling linseed oil with a large proportion of driers, and mixing with turpentine. It mixes with paint readily and is efficient.

836. Pigments are finely divided, insoluble, colored powders, yielding paints when mixed with suitable media. They must have (1) body or opacity to conceal the surface; (2) covering power; (3) drying quality; (4) durability; (5) color.

Amorphous powders have greater body than crystals and therefore, greater covering power. The drying power depends upon the power of oxidizing, or promoting oxidization of the vehicle. The permanency is the power to resist the action of the sun, air, water, gases, vapors, acids, etc. The color depends upon the chemical composition, the molecular constitu-

tion, the physical condition, the mode of production, washing, etc.

837. White Pigments. White lead (\$459 ff.) is the most common white pigment. This is a basic carbonate of lead. The hydroxyl of the compound combines with the oil forming a white elastic coating, and the CO_2 gives opacity. It is frequently adulterated with barium sulphate, chalk, calcium sulphate, clay, lead sulphate, etc. The great objections to the use of white lead are that it is poisonous and that it darkens when exposed to the action of hydrogen sulphide. There are many substitutes for white lead on the market, those above and zinc oxide, zinc sulphate and zinc sulphide being the most common. These are used either with white lead or without it, and are often mixed together in varying proportions.

Lithopone, called also lithophone, Orr's white, Charlton white, or Beckton white, is approximately 70.5% barium sulphate and 29.5% zinc sulphate, and prepared by precipitating barium sulphate with zinc sulphate, washing, pressing, drying and firing. It is not affected by hydrogen sulphide and has considerable body, permanency and fineness of tint. Sulfozone is similar, consisting of zinc sulphate and calcium sulphide.

Sublimed white lead is about 75% lead sulphate, 20% lead oxide, and 5% zinc oxide. It shows absence of crystals and remarkable uniformity of grain. It makes a very durable paint.

Different Names are often applied to the same pigment. Very fine white lead, when pure is known as Flake white, Berlin white, Silver white, and Krems white. Venice, Hamburg and Dutch whites are mixtures of white lead and barium sulphate in different proportions. Blanc fixe, Baryta white, Fast white, and Permanent white are barium sulphate. Strontium white is strontium sulphate. Magnesia white is a mixture of magnesium oxide and magnesium carbonate. Calcium carbonate is known as Spanish white, Paris white or whiting. Zinc oxide is called zinc white or Chinese white. This substance is increasing in favor and has a fair covering power. It does not change

color in the presence of hydrogen sulphide, since the zinc sulphide produced is white. It can be used with either oil or water and is non-poisonous. Calcium sulphate is said to increase its covering power.

838. Yellow Pigments including the yellow ochres, Stone yellow, Roman yellow, mineral yellow, etc., are argillaceous earths containing varying proportions of hydrated ferric oxide, and are very durable and trustworthy. Salts containing chromium are used in a large number of yellows. Among these are Siderian yellow, $\text{Fe}_2(\text{CrO}_4)_3$, chrome yellow, or lead chromate, PbCrO_4 , or the latter substance mixed with lead sulphate. Orange chrome yellow is lead chromate with lead oxide, $\text{PbCrO}_4 \cdot \text{PbO}$. Cologne yellow is a mixture of lead chromate, lead sulphate and calcium sulphate. The chromates of strontium, barium and zinc are durable but have little body. Lemon yellow is barium chromate and is one of the most important of these compounds.

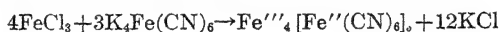
839. Red Pigments. Among these are Vermilion or cinnabar, HgS , which is moderately permanent in oil, but is too expensive. Minium or red lead, Pb_3O_4 , is not permanent. Indian red, Venetian red, rouge, colcothar, and bole are ochres and durable. Chrome red, a basic lead chromate, and chrome orange, a mixture of normal and basic lead chromates, are both unstable. Vandyke red is copper ferrocyanide, $\text{Cu}_2\text{Fe}(\text{CN})_6$.

840. Green Pigments include many of the salts of copper such as malachite or mountain green, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$; Schweinfurt or emerald green (copper aceto-arsenite) $3(\text{CuAs}_2\text{O}_4) \cdot \text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$; Brunswick green (copper oxychloride) $\text{CuCl}_2 \cdot 3\text{CuO} \cdot 4\text{H}_2\text{O}$; verdigris, (copper basic acetate) $2\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{CuO} \cdot 6\text{H}_2\text{O}$; and Scheele's green, a basic arsenite of copper, now little used. All copper greens are darkened by hydrogen sulphide and are poisonous.

Chromium compounds used as greens are permanent and full bodied. Guignet's green, chrome emerald green etc., are hydrated sesquioxides of chromium with the phosphate or

borate of chromium. Rinmann's green, cobalt green or zinc green are cobalt oxide with zinc oxide. There are many unstable greens of vegetable origin, but they have little value as pigments.

841. Blue Pigments. One of the most important of the blues is Prussian or Berlin Blue. This may be formed by the addition of a ferric salt solution to potassium ferrocyanide, when a dark blue precipitate will be obtained. It is rather hard to free the precipitate from potassium salts, but the equation for the reaction may be written



Prussian blue has a deep greenish-blue tint, there being no other blue having either the same depth of color or the same shade or tint. When dry it has a bronzy appearance, which is greatest when the blue is pure and this is especially characteristic of Chinese blue. Prussian blue is exceedingly hard and difficult to grind, but in order to develop its coloring powers to the greatest extent it must be ground as fine as possible, and this naturally leads to the use of blues more easily ground, such as Brunswick blue. The latter is made from barium sulphate by the addition of iron sulphate and potassium ferrocyanide, the depth of color being dependent upon the amount of the iron and potassium salts used. Antwerp blue is a light tinted Prussian blue.

Indigo, $\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_2$, is a vegetable color and fades on exposure.

Native Ultramarine is pulverized lapis lazuli. It is an excellent and stable color but is costly. Artificial ultramarine is composed of the silicates of aluminum and sodium with sodium sulphide. It is nearly equal to the native compound, and much less expensive. The formula for the artificial ultramarine is $\text{Na}_4(\text{NaS}_3\text{Al})\text{Al}_2(\text{SiO}_4)_3$. Both the native and the artificial ultramarines are permanent in the absence of acids.

Cobalt blue is an aluminate of cobalt. Smalt, zaffre, royal and Saxony blues are glasses colored by cobalt oxide. Copper blues are of little value.

842. Brown Pigments. Vandyke, Rubens, Cassel and Cologne browns are partly vegetable. They are prepared from peat, cotton, soot, etc., and bituminous matter is often present. There are several Vandyke browns, but only those prepared by calcining highly ferruginous brown ochres, or consisting of a dark tinted form of colcothar are permanent. Burnt sienna and raw and burnt umber are earths used either in the raw state or calcined. Most of them are durable and reliable. There is no standard composition for these compounds, but they owe their color to limonite, a hydrated oxide of iron. This is mixed with aluminum silicate, lime, barium sulphate, etc. The amount of iron present is not as important as its physical condition, how it is combined with the other substances, etc., the amount varying from 11 to 33%. The ochres are among the most durable pigments. They do not affect other pigments and are not affected by them. They can be used in all vehicles and for all kinds of work. When the ochres are heated the color turns to red and they are then sold as Venetian red, Indian red, etc. The change of color is due to the passage of the iron compounds from the hydrated to the anhydrous condition. Siennas resemble the ochres, but are browner in color, due to limonite. They also contain a little manganese and organic matter.

843. Black Pigments. Ivory black, bone black and lamp black are more or less pure carbon. Blue black, Frankfort black and drop black are made from vine twigs, ivory cuttings, bone shavings, peach stones, etc., and are calcined until completely charred. Manganese black is made from manganese dioxide. All of these blacks are very durable.

In General the ochres, lamp black, red lead, white lead, zinc oxide, Prussian blue, barium sulphate, chrome yellow, orange and red, vermilion and the commoner copper greens are the most important in house paints. White lead is usually present in the greatest amount and the others are known as stainers. All compounds of copper, lead, bismuth and some of mercury darken when exposed to the action of hydrogen sulphide. Colors

that are in part or wholly of organic origin fade on exposure by oxidation. Those not affected by water, such as barium sulphate and zinc oxide, usually have less covering power.

844. The following shows the composition of two paints as stated by the manufacturer:

I. Lemont stone	
Pigment	59.10%
Liquid	40.90
Pigment contains	
Sublimed white lead . . .	46.97
Zinc oxide	44.92
Calcium carbonate . . .	4.92
Coloring matter	3.19
The liquid portion contains	
Turpentine and Japan drier	11.79
Linseed oil	88.21
The tinting colors are	
Yellow ochre	
20% ferric oxide	
80% aluminum silicate	
Lamp black	
II. Porch gray	
Lead	23 85%
Zinc oxide	22 85
Calcium carbonate	2.50
Naphtha	6 38
Varnish	15.95
Japan drier	9.90
Coloring matter26
Linseed oil	18.31
The tinting colors are	
Chrome yellow, PbCrO_4	
Carbon (Lamp black)	

845. **Miscellaneous Paints.** *Distemper Painting* is a term applied to the painting of absorbent surfaces, such as plaster.

This work requires a priming of white lead, or whiting ground in water and mixed with a little glue.

Luminous Paints depend for their action upon the presence of phosphorescent sulphur compounds of strontium, barium or calcium, sometimes with bismuth, tungsten, etc. These are calcined and mixed with the medium. Calcium tungstate gives a powerful luminous paint. Special luminous paint for watch hands and dials is described in Chapter 23.

Fire-proof Paints all contain asbestos, while many of them contain alkaline silicates, borax, fluorspar, glass, etc.

Water-proof Paints contain lime, crushed flint and marble, sawdust, shellac, asphaltum, gutta percha, residues from petroleum distillation, etc., in addition to, or as a substitute for, some of the ingredients of ordinary paints.

Anti-fouling, Anti-corrosive, or Preservative Paint for the bottoms of ships, iron surfaces, etc., contain resinous constituents and resemble varnishes. Iron oxide, pitch, shellac, colophony, tannin, silicates, etc., are common ingredients. An emulsion of tar and clay is said to be a highly protective coating for iron and wood.

Washable Paints. Most distemper paints are not washable, but if sodium silicate, casein, butter-milk, or other similar substance is added, and the miscibility is increased by the addition of soap, the paints are washable when dry.

Enamel Paints are brilliantly colored, yielding smooth and lustrous coatings. They consist essentially of an oil varnish ground up with finely divided pigment and thinned by turpentine.

Special Paints include gold, silver, aluminum and other paints. Gold paint is bronze powder in a solution of celluloid in amyl acetate and acetone while in aluminum paint, now widely used, finely powdered aluminum takes the place of the bronze powder.

846. *Varnishes* are liquid bodies which, when applied to a surface by means of a brush, dry more or less quickly, and leave

a highly lustrous coat of a very durable character. There are two kinds of varnishes, *oil varnishes and spirit varnishes*. Oil varnishes are exceedingly durable but are slower in drying than the spirit varnishes, the latter making use of more volatile solvents.

The materials used in making varnishes include drying oils, solvents or thinners, gums, driers and coloring matters.

847. Gums include all exudations coming from various trees, first as a liquid, that soon sets into a more or less hard mass, but there are at least three divisions of gums—(1) Gums proper; (2) Resins; (3) Rubbers. Among the gums of the first class are gum acacia, or gum arabic, the best varieties being used for pharmaceutical preparations, confectionery and other purposes, while the common varieties are used for mucilage, varnish making and in the textile industry; *gum tragacanth*, not suitable for varnishes, but used in pharmacy, in calico printing, etc.; *British gum* or *dextrin*, prepared by heating starch, either alone or with a small quantity of acid, dries with a fair amount of gloss and used to some extent in making water varnishes.

848. Resins are the most important materials for varnish making, some being used for no other purpose, while some are not suited for the work. They are usually more or less hard, brittle, lustrous, generally clear and transparent, insoluble in water, but soluble in alcohol, ether, benzol, and other similar solvents. Their composition is very complex, and not well known, but they are known to be very rich in carbon, poor in oxygen, and without nitrogen.

Resins occur in various forms, in knotty masses, as copal, animi, dammar, etc.; in drops, as mastic; in tears or cylindrical pieces, as sandarac; while others come into the market shaped artificially, as gamboge, in cylinders; shellac, in thin plates; dragon's blood, in thin sticks or powder; benzoin and elemi, in blocks.

The Color of Resins in general is pale brownish, but acceroides is deep yellow, copal is brownish yellow, dragon's blood is red,

shellac is orange, dammar is almost colorless, elemi is usually of a grayish tint, asphaltum is dark brown, approaching black.

The Hard Resins such as hard copals, animi and amber are difficult to melt and make the best varnishes, very fine and durable, but difficult to make. Elemi will bend between the fingers and soften from the heat of the hand. Animi and amber are difficult to break up and when made into a varnish will stand a great deal of hard usage, while accroides and rosin are brittle and easily reduced to a powder and will not stand much wear when made into a varnish.

849. Spirit Varnishes are made by dissolving the resinous material if used alone in methylated spirit, benzol, turpentine, or coal-tar naphtha. The mixture is stirred, without heat until dissolved. Usually from 2 to 4 pounds of the resins are dissolved in a gallon of the solvent.

850. Oil Varnishes are much more difficult to make. The resins, such as copal, animi, amber, kauri, rosin, etc., are melted over a furnace in a copper "gum pot" with constant stirring, great care being used to have all of the gum melted, but without raising the heat too much. Some decomposition of the gum occurs and there is a loss of 15 to 25% of the weight of the gum. Good linseed oil is heated to 260° C. and poured into the melted resin with constant stirring, and keeping the temperature well up to this mark for several hours, until a little taken between the finger and thumb can be drawn into long strings. It is then allowed to cool to about 130° and turpentine is added to make it fluid and of the right consistency. The varnish is then stored in tanks for several months to allow the materials to become properly mixed and to clarify, all the solid materials settling to the bottom.

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Jennings	Paints and Varnishes	Pitman
Laucks	Commercial Oils	Wiley
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CHAPTER XXXV

PAPER AND INK

851. Raw Materials Used in Paper. The raw material used in the manufacture of paper is cellulose, derived from rags or from wood pulp. Straw is used for some of the cheaper grades of paper, and jute and manila hemp for tough wrapping paper.

852. Preparation of Rag Pulp. The best grades of paper are made from rags. The rags come to the papermaker sorted into grades. These are picked over and resorted more carefully, and all buttons, rubber bands, and other foreign material are removed. They are next run through a shredding machine which cuts them into small pieces, about an inch square. After having all the dust and loose dirt blown out of them, they are next conveyed to the rag-cooker, a large cylindrical tank which can be sealed shut. Here a mixture of sodium carbonate solution and slaked lime is added, giving an alkaline strength of 1 to 5% and the rags are digested under a steam pressure of 5 to 60 pounds for some time. This treatment removes any pieces of wool or silk which may have been in with the cotton or linen rags, and serves to loosen up the dye and to make the bleaching much easier. After this treatment the resulting pulpy mass is washed to remove the alkali, and it is ready for the bleaching process.

853. Preparation of Wood Pulp. Wood is the most common source of pulp for paper making. The annual production of wood pulp now reaches about 6,000,000 tons about half of which is made in Canada and the United States. Mechanical pulp is the cheapest grade and the most quickly made. "Chemical pulp" produces a much better grade of paper making material. Fig. 200 shows the splitting of pulp wood for paper making.

854. Mechanical Pulp is prepared by grinding up the wood. This is done by forcing the wood against revolving grindstones, which reduces it to a mass of wood fibers. In the cold process

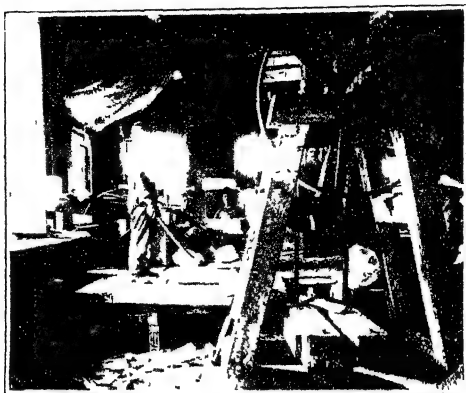


FIG. 200. Splitting Pulp Wood for Paper Making

much water is used, which keeps the stone cool and carries away the fibers. If the quantity of water is reduced there is a considerable rise in temperature due to friction, and the product is "hot ground pulp." The two processes give products of very different character, the fibers in the "hot ground pulp" being much longer, which results in a coarser pulp. The pulp thus produced is screened to remove coarse material, pressed to remove excess water, and formed into sheets for shipment to the paper mill.

Pulp made by this process contains all of the non-cellulose material found in the original wood. It rarely contains more than 55% cellulose, and its use is confined chiefly to the manufacture of the cheaper grades of paper.

855. Chemical Pulp is the name given to pulp prepared from wood chips, which have been treated with various reagents to dissolve the non-cellulose constituents, leaving a residue of

impure cellulose. The resulting pulp has a composition quite different from the original wood. It usually contains about 90% cellulose, and it makes a very good grade of paper. Chemical pulp is classified according to its method of preparation into "sulphite pulp" and "soda pulp."

856. Sulphite Pulp. In the sulphite process wood in the form of chips is digested in a solution of calcium bisulphite in a closed vessel under pressure for a considerable period of time. The calcium bisulphite is prepared by passing sulphur dioxide into a suspension of calcium hydroxide. The resulting solution contains an excess of free sulphurous acid. Under this treatment the non-cellulose constituents of the wood are dissolved, leaving a fairly pure cellulose. After a thorough washing the pulp is ready for the paper mill.

Recently attempts have been made to utilize the waste sulphite liquor. It contains many organic compounds of a ketonic structure. On neutralizing with lime, aerating, and adding yeast, fermentation sets in, resulting in the production of alcohol. On distillation about 15 gallons of alcohol per ton of cellulose are obtained.

857. Soda Pulp. In the soda process the wood after coming from the wood chipper is digested in sealed tanks with a solution of sodium hydroxide containing about 8% of sodium hydroxide. Steam is used for heating and a pressure of 120 pounds is maintained for several hours, which gives a temperature of 170° C. Under such treatment the sodium hydroxide dissolves the organic acids, resins and other non-cellulose substances and leaves a residue of nearly pure cellulose which has a brown color. The sodium hydroxide used, is usually prepared from the action of sodium carbonate on slaked lime. The spent liquor is evaporated to dryness and calcined. The resulting ash contains about 50% of sodium carbonate, which is dissolved out, and mixed with lime for use again.

858. Bleaching. Bleaching of paper pulp produced by any process, is brought about through the use of bleaching powder,

or solutions of sodium hypochlorite, produced by the electrolysis of sodium chloride. In either case the hypochlorous acid produced through the decomposition of the hypochlorite is the active bleaching agent. The oxidizing action of this compound converts the colored organic compounds in the pulp to colorless ones. After bleaching, the pulp is carefully washed to remove all traces of the bleaching agents.

The amount of bleaching powder required is 7% for straw to 15% for wood, based upon the unboiled material. Chlorine will not bleach the majority of pulps, because it enters into combination with the fibers, producing yellow colored combination products. Magnesium hypochlorite, produced by the electrolysis of magnesium chloride, is being used for bleaching and is said to have a considerably greater bleaching power than calcium hypochlorite.

859. The Beaters. In the paper making process the pulp now passes to the beaters. These are large oval tubs about twenty feet long, divided into two channels by a central partition or "midfeather." On one side is a large roll bearing on its circumference a series of knives which mesh into a similar series on the bottom of the beater. The pulp mixed with much water is driven around and around the tub passing between these knives until the fibers are completely disintegrated. During this process filler, size and color are added and thoroughly mixed in. See Fig. 201.

860. Fillers. China clay and talc are the common fillers employed. They are used to fill up the spaces between the fibers in the paper sheet and to make it opaque. Since the fibers have high absorbing power, it is necessary to cover them with a nonabsorbent coating if ink is to be used upon it. The materials most commonly used for sizing are rosin soaps, starch, casein and glue. The rosin size is a soap made by boiling rosin with sodium carbonate. To every hundred pounds of wet pulp about two and a half pounds of rosin size and five pounds of filler are added. After a thorough mixing in the beater a solu-

tion of alum is added. The excess sodium carbonate present in the rosin size precipitates aluminum hydroxide. The aluminum hydroxide, being a colloid, precipitates both the suspended filler and the size upon the fibers. If it is desired to color the paper the color is added at this stage also. Most bleached pulps have a slight yellow tinge which is removed by adding some form of blue, such as ultramarine, smalt or aniline; or pink, such as cochineal or aniline. If it is desired to have a colored paper such substances as Prussian blue, chrome yellow, Venetian red, etc. are added.

In its passage to the paper making machine the pulp usually passes through a "Jordan engine." This machine is made up of a cone shaped plug about five feet long, which fits into a hollow

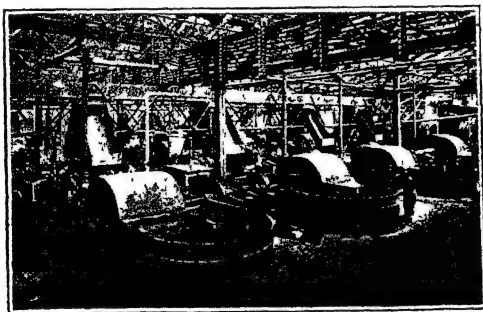


FIG 201. Beaters for Making Rag Pulp.

cone in which it revolves. The surfaces of the plug and the cone are both fitted with steel bars between which the pulp receives a final grinding.

861. The Making of the Sheet. The most common type of paper making machine is the Fourdrinier machine. The essential parts of this machine are the flow box, which contains the pulp suspended in water, the screen, on which the sheet is formed, and the dryers.

The flow box to which the prepared pulp has been pumped, is mounted above one end of the screen. Slots in the bottom about

one tenth of an inch in width allow the pulp to flow upon the screen. This screen is an endless belt of finely woven bronze wire. Its width depends on the width of the web of paper desired, usually from thirty six to two hundred inches. As the screen moves rapidly under the slots in the flow box, the pulp is deposited in a uniform layer upon it, the water drains through, and owing to a lateral vibratory motion the fibers become



FIG. 202 Bleaching Paper

bleaching and drying of paper.

meshed into a tough sheet. As the screen moves forward, the water having drained out, the sheet becomes sufficiently firm to be taken from the screen and passed through the dryers. These are large hollow steam heated iron rolls, varying in number with the weight of the paper, from 10 to 60. The wet web of paper passes around these heated rolls, and the water in it is removed by evaporation. Figs. 202 and 203 show the

862. Wove and Laid Paper. The frame in which the pulp is first caught, or the surface upon which the pulp is fed determines the texture of the paper. If the surface is smooth and even, composed of felt or blanket, the paper will be of uniform texture throughout, showing no light and dark figures when held against the light. This is called wove paper. If the frame is of fine wire netting, the paper will show little light dots or points, very close together, and is called wire wove. If the frame is composed of parallel wires it is evident that a greater

thickness of paper will be produced where more pulp settles between the wires. When such paper is held to the light it will show alternate light and dark lines, and is known as laid paper. When there are only a few light lines the paper is known as batonne paper. The laid lines may form geometrical figures, such as squares, rectangles, diamonds, etc., or may be wavy, and to such types the term quadrille paper is often applied.

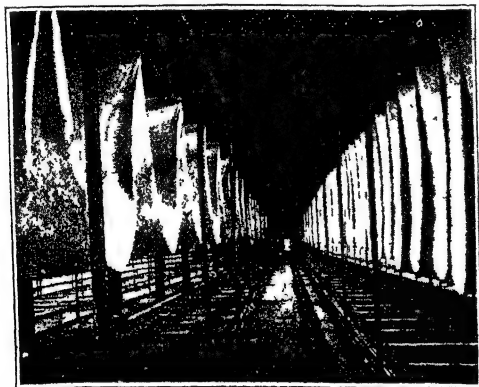


FIG. 203. Drying Paper

863. Watermarks are small designs, such as stars, anchors, crowns, flowers, letters, figures, etc., formed from wire or cut from metal and soldered to the frame on which the pulp is caught. The action of these is precisely similar to that of the wires causing the laid lines. Sometimes the watermark is very distinct and may be seen by holding the paper to the light. Again the watermark may be faint, or if the paper has printing on one side may be invisible to the naked eye. The watermark may be detected by placing the paper, printed side down, upon a black surface and covering it with a few drops of deodorized benzine or gasoline. The watermark will then show as dark lines against a lighter background.

864. The Calender Rolls. The final step is the calendering process. To give the paper a smooth finish or a polish it is run through a series of rolls arranged in a vertical stack. The bottom roll is under very heavy pressure, sometimes as much as 40 tons. The bottom roll is directly driven by being coupled to a motor; so there is considerable friction due to the inertia of the other rolls resting on one another. This friction, together with the heat which it produces, acting on the size and filler pro-

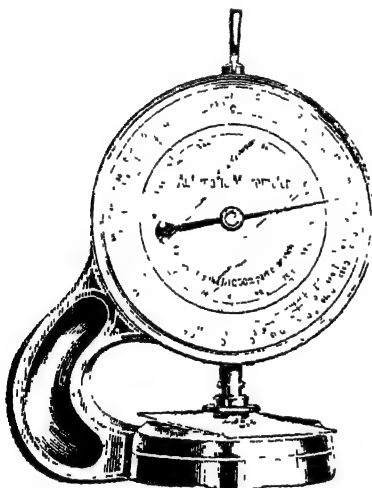


FIG. 204. An Accurate Machine for Determining the Thickness of Paper.

duces a high gloss on the surface of the paper. In the preparation of coated paper, before passing through the calender rolls, the sheet is given a coating of China clay, barium sulphate, casein, or other coating material. Paper thus treated has a higher gloss and a finer finish than one that has not been coated. The paper is next wound into rolls or cut into sheets and is ready for the market.

In buying paper it is often desired to test the paper for breaking strength, thickness, weight per sheet or ream, etc. Fig. 204 shows a micrometer for measuring thickness, and Fig. 205 shows a scale for determining weight directly from the weight of a small sample cut to a standard size. The graduations give the weight in pounds per ream.

865. Filter Paper is composed of very pure cellulose. It is made in many different grades for different methods of filtering. For rapid filtering a more porous paper is used, especially if the suspended particles are not very fine. Hard, thin papers of close

texture are used for fine precipitates. For quantitative work papers washed in hydrochloric acid, or both hydrochloric and hydrofluoric acids are used, especially in combustions. The weight of the ash from a single paper is stated on the package, so that allowance may be made for it. Filter paper is sometimes hardened by treatment with nitric acid, which gives it a hard, smooth surface, very tough, and able to withstand considerable pressure as in vacuum work. Filter paper may also be hardened and toughened by treatment with dilute sulphuric acid, often called parchmented paper. Concentrated acid, however, destroys the paper, by removing the water, leaving the black particles of carbon, just as when the acid acts upon any other form of carbohydrate.

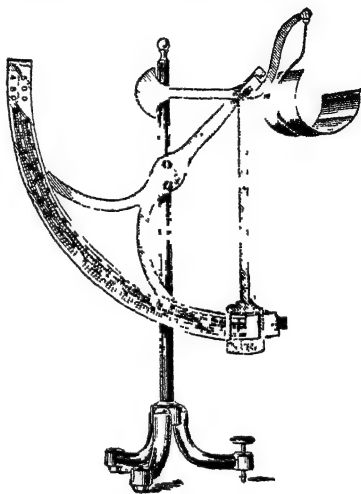


FIG. 205 A Machine for Determining the Weight of Paper by the Sheet or Ream.

INKS

866. Inks Containing Gallic or Tannic Acid. Although there are a great many varieties of ink on the market, one of the most widely used kinds depends for its color upon the formation of iron tannate or iron gallate, produced by the action of tannic or gallic acid upon a solution of an iron salt. Gall nuts contain gallotannic and gallic acids, and either these or some similar substance, will yield the acid when covered with warm water, and allowed to stand. One formula calls for galls, 1200 parts by weight; ferrous sulphate, 800 parts; gum arabic, 800 parts;

water, 24,000 parts; creosote, 3 parts. The crushed galls are covered with part of the water; the other ingredients are dissolved in the rest of the water, then poured over the galls and the mixture is allowed to stand for three weeks. A finer color is produced by adding a piece of mouldy bread to the galls, so that they will ferment, and allowing them to stand for 8 to 10 days when boiling water is added to stop the fermentation. The liquid portion is drawn off and added to the other materials and after a week or 10 days the ink is ready for use. Logwood may be substituted for all or part of the galls.

In oxidized inks the iron may exist as $(C_{14}H_9O_9)_3$. Fe. $Fe(C_{14}H_9O_9)_3$.

867. Inks Made From Aniline Dyes are commonly known as writing fluids. They may be obtained in all colors, and if the correct shade and quality of dyes are obtained the ink may be made easily by dissolving the dye in water, either with or without boiling and filtering, depending upon conditions. When properly made they are fast and permanent, flow freely and give a fine color. The aniline colors are described more fully in Chapter 31.

Copying ink and hektograph ink contain aniline colors. They are used for making copies from an original. As an example of hektograph ink 10 parts of water soluble blue and 10 parts of glycerine may be dissolved in from 50 to 100 parts of water.

Red ink usually consists of eosine, magenta, or some other aniline color dissolved in water. It is easily and cheaply made, but usually sells for a higher price than ordinary ink.

868. Indelible Inks are those that have great durability under all conditions. They consist, for example, of India ink or lampblack held in suspension in glutinous or resinous liquor, such as lampblack in sodium silicate. Indelible pencils may be made in part from methyl violet. When moistened they form small amounts of methyl violet ink.

Other permanent inks are made in other ways. Vanadium ink is made by adding a small proportion of ammonium vana-

dinate to a filtered concoction of galls. It is very permanent and requires the destroying of the paper to remove the ink.

Chrome ink is made by adding 1 part of potassium chromate to 1,000 parts of a saturated solution of logwood, containing 22 pounds to 14 gallons. The chromate should be added gradually with constant stirring. The addition of gum is harmful.

Safety writing ink for checks may be made by dissolving 320 grains of ferric ferrocyanide, 30 grains of oxalic acid, 10 grains of magnesium sulphate and 30 drops of Turkey red oil in 1 quart of water.

869. Fugitive Inks are inks that wash out easily, showing at once if the writing has been tampered with. Such inks are used for printing in faint letters the full face of a check, or part of the design of a postage stamp. When moistened the ink disappears or blurs in such fashion that the article is worthless. One substance that may be used for such purpose is cobalt sulphocyanate, which gives a rich dark blue color when concentrated, but disappears at once when wet with water. Similar to this is cobalt chloride often used for sympathetic ink. (See §437.)

870. Printer's Ink, when made in the most approved manner, consists of lampblack in linseed oil varnish, but many cheap substitutes are offered. Oils or resins with soap are used instead of linseed oil, or mineral oil, rosin oil, etc., are substituted. Printer's ink may be colored white by the use of barium sulphate instead of lampblack; red by the use of orange lead, vermilion, burnt sienna, Venetian red, etc.; yellow by lead chromate, yellow ochre, etc.; blue by cobalt, Prussian blue, indigo, Chinese blue, or ultramarine; green by chrome green, cobalt green or by mixtures of yellow and blue; purple by mixtures of red and blue; deep brown by burnt umber and a little scarlet lake; lilac by cobalt blue with a little carmine; pink by carmine or crimson lake. The use of bronze, gilt and aluminum powders applied to the fresh inked surface of the finished printing gives a fine metallic finish.

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CHAPTER XXXVI

LEATHER AND TANNING

871. Tanning consists of treating animal skins with certain infusions of vegetable tannins so as to change the gelatinous tissues into a tough, non-decaying substance, known as leather.

Fresh hides and skins contain from 50 to 70% of water and in order to reduce the weight may be dried. As hides reach the tanner they may be fresh, dried or salted, either with or without the addition of arsenic trioxide to prevent the ravages of insect pests.

872. Preliminary Treatment. The hides are first freed from blood and dirt and softened. This latter operation is easier with fresh hides than with those that have been dried. If hides are soaked in plain water for softening, a tough hide may require two or three weeks of continuous soaking in water that is not changed frequently before becoming soft. The water that is used for a long time contains much organic matter from previous soakings but it is not good for the leather, since it destroys the tissue and softening may be brought about by very dilute sodium hydroxide, sodium sulphide, weak organic acids, or 1/40 normal sulphurous acid. When the hides have been softened so as to bend without breaking they are worked in a mechanical manner so as to soften them still further, either by pounding, churning or kneading.

873. Depilation, or the removal of the hair, is brought about in different ways. The sweating process is essentially putrefaction. The hides are placed in a warm room at 15° to 20°. The air is saturated with moisture and steam is admitted. After a lapse of 3 to 7 days the hair is softened enough so that it may be scraped off. *Liming* may precede scraping, and not only stops putrefaction, but causes a slight plumpness. The hair

is also removed by liming, the hides being suspended in the lime pits for 4 or 5 to 14 days, and rocked or shaken. Hair may be removed readily if the hides are placed in fresh lime for 1 to 4 days and then soaked in water at a temperature of 40° to 50° for some hours.

Other Stronger Alkalies for dehairing are not better, because they form compounds not easily removed until neutralized by acids, and the grease is not saponified but emulsified. It is easy to spoil hides by using the strong alkalies and acids, but it is almost impossible to spoil hides with lime. If 2 to 4 pounds of sodium sulphide are dissolved in water and the whole thickened with lime to a soupy consistency the mixture will remove hair in a few hours, but this is not considered good for the best quality of leather. Sodium sulphide may also be added to the lime pots, $\frac{1}{4}$ to $\frac{1}{2}$ pound per hide being used for quickening the process. A recent process calls for the use of liquid air. The hides are suspended in the liquid for a few seconds and the frozen hairs are scraped off, leaving the roots in the skin.

874. Bateing and Drenching. The lime is removed from the hides with water, and then with very dilute sulphuric acid, keeping the hides in constant motion and avoiding an excess of acid. *Bateing* (abateing) or reducing the plumpness of the hide is necessary in light leathers. For this purpose an infusion of pigeons', hens' or dogs' dung, or bran, or both is used. The action is said to be due to bacteria. An artificial bate, known as "erodin," consisting of a carefully prepared culture of bacteria and a dry powder may be used instead.

875. Tanning Materials. Tannin or tannic acids will precipitate gelatin from a solution as an insoluble compound. Tannins contain pyrocatechol, $C_6H_4(OH)_2$, or pyrogallol $C_6H_3(OH)_3$, or an isomeride of the latter, known as phloroglucinol. Different tannins act differently upon leather. They are hard to separate, are non-volatile and do not crystallize.

Oak bark is one of the oldest and best of the tanning materials

It is somewhat slow, since it contains only 8 to 12% of tanning material, but produces excellent leather.

Valonia contains up to 35% of tannin. It is similar to oak bark and gives a heavier leather.

Myrobalans contains 25 to 35% of tannin and is good to mix with hemlock extract.

Divi-divi contains 30 to 50% of tannin. It is similar to valonia and produces a heavy leather, but is liable to decompose and produces red stains.

Sumac contains from 20 to 30% of tannins and is similar to myrobalans. It is used chiefly for light leathers or to brighten the colors of heavy tannins.

Mimosa bark, found chiefly in Australia, contains 20 to 40% of red tannin, from pyrocatechol, and gives considerable weight and firmness to the leather.

Hemlock bark contains 8 to 10% of tannin, while the extract contains 20 to 30%. It is similar to Mimosa bark, but gives a larger percentage of red anhydrides, and therefore, a heavier leather, with a more pronounced color and less easily modified by other agents. It is used to a large extent in the United States.

Quebracho wood is found in Argentine Republic and elsewhere in South America. It contains about 20% of rather difficultly soluble catechol. It is used largely as extracts which are decolorized and rendered more soluble by bisulphites.

Mangrove barks, from the East Indies, are used chiefly as extracts. They contain up to 40% of dark red, but fairly soluble, catechol tannin.

Gambier, also found in the East Indies, contains 30 to 40% of catechol tannin. It penetrates rapidly, but has less astringency and adhesive power than other tannins. Used alone it gives an inferior leather, but it may be used with other tanning agencies. In general, it does not contract or draw the grain very much.

876. Preparation of the Tanning Material. Most tanning materials are ground and exhausted by water to save shipments

of useless materials. The dark color and insoluble matter are often removed by precipitation with blood or blood albumen, dissolved in a warm infusion and then heated above the coagulation temperature. Metallic precipitants are sometimes used. Sulphurous acid and bisulphites are used for bleaching the tanning liquor, and to make the reds more soluble. The extracts are then concentrated in vacuo until they contain 50 to 60% of water if they are to be sold as a liquid extract, and 20 to 25% if they are to be shipped in a solid condition.

877. Sole Leather is Made by *plumping*, either with lime during depilation, or if the latter process is accomplished by sweating, the plumping is done by the use of sulphuric acid. When a hide swollen with lime is brought into the tanning liquors the weak acids present rapidly neutralize the lime (alkali), and the hide, previously plump and firm, becomes soft and flaccid and decreases in thickness. If only a little acid in proportion to the tannin is present this action is very gradual and the tannin, which penetrates rapidly in an alkaline condition of the hide, fixes the fiber in a swollen condition and a plump, rapid tannage is obtained, often deficient in color from the tendency of the lime to form tannates which darken on drying. If only a little lime is present and the acid predominates over the tannin, the tissue, at first soft and flaccid, swells gradually and combines with the tannin in an acid condition, producing a plump leather of good color. But if an unswollen hide comes into the liquors with insufficient acid, or if plumped with lime and allowed to fall back, the tanning will fix it in the fallen condition and thick leather cannot be made.

878. The Tanning Liquors are placed in deep pits in which the hides may be suspended without touching, and where they may be kept in motion for at least a day. The hides color rapidly and must be moved forward gradually into stronger liquors. After the color is fully set the hides are laid in pits, either with tanning liquor alone, or with a little of the solid material dusted between them. The hides are handled once a

day or oftener and when colored quite through are placed in layers in stronger liquors and solid tanning material, such as mimosa bark, oak bark, myrobalans or valonia, is strewed between them, where they are allowed to remain undisturbed for one to six weeks. They are then raised, drained, and washed, or bleached with bisulphited (bleaching) extract. The hides are then slightly oiled and hung in a loft until about half dry. They are next laid in a pile to equalize the moisture, and the grain is struck out, usually with a machine. They are again slightly oiled, somewhat further dried, rolled twice and dried in a warm loft. (Fig. 206.)



FIG. 206. Rolls of Leather in the Drying Room.

879. Enameled, Patent, or Japanned Leather. The hides must be well freed from grease before tanning, often by the use of benzine, and but little oil may be used. The hides are stretched on boards or frames and coated with a linseed oil varnish boiled with Prussian blue and sometimes with lampblack or other pigments. The black color is brought about by the iron in the Prussian blue, which also acts as a drier. The coating is dried at 70° to 80°, smoothed with pumice, and other coats applied until the right thickness is obtained.

880. Morocco is made from goat skins, the rough haired seal, or inferior kinds from sheep skins. After dehairing by lime, bateing, and drenching, they are tanned with sumac. When tanned they are dyed with aniline colors or dye woods, glazed with albumen, and an artificial grain is given by engraved or electrotyped rollers.

881. Chamois or Wash Leather is made from sheep skins, thoroughly limed, to dissolve the cementing material and to

produce softness. The lime is removed by a bran drench, and after the moisture is pressed out, the skins are oiled with fish oil or whale oil, folded into cushions and worked under fulling stocks for two or three hours. They are then hung up to cool and to dry partially. This process is repeated many times until all of the water has been replaced by the oil. The skins are next laid in piles where fermentation occurs with the evolution of considerable heat, owing to the oxidation of the oil, and the yellow color is produced. It is not known just what chemical change takes place in the fibers but it is said to be due to aldehydic products of the fatty acids and glycerol. Chamois is resistant to boiling water, to acids and to alkalies. An excellent leather resembling chamois is produced by treating the skins directly with formaldehyde, and some of the other aldehydes in a solution rendered alkaline by sodium carbonate.

882. Kid. Glove kid is produced from kid skins and fine lamb skins. The cementing material must be removed so as to render the leather soft and pliable, giving free movement of the fibers in stretching. Calf skins are usually dehaired by liming, and kids by liming with the addition of red arsenic sulphide. After bateing and drenching they are thoroughly worked to get rid of the fat glands and scud. They are tanned by placing them in a drum containing flour, alum, salt and egg yolk with the addition of olive oil. They are then dried, softened, and aged by keeping them in a cool warehouse for several weeks. Calfskin is then dampened, shaved on the flesh side and dyed black. A mixture of ammonia, potassium dichromate and logwood may be used, the color being darkened and fixed by a bath of ferrous sulphate. The leather is then re-egged, worked with a knife, rubbed with a mixture of wax, soap and gum, and ironed. Kid glove leather usually has a second feeding in the drum with egg yolk and salt. The leather is dyed all shades with berry juices brightened with aniline. The finishing consists of wringing out, drawing over a blunt knife and drying.

883. Chrome Leathers have a much greater resistance to hot and cold water than those prepared with aluminum salts. It is possible to produce the desired results with chrome alum and salt.

In the two bath chrome tanning the hide is treated with chromic acid, made by the action of hydrochloric acid upon potassium dichromate or sodium dichromate, and afterwards with a solution of sodium thiosulphate and hydrochloric acid. The hide takes up the chromic acid, and this is converted into the basic condition by the action of the thiosulphate. It is then "fat-liquored" with a thin emulsion of oil and soap, dyed, dried and softened.

In the one bath chrome tanning, the hides, after coming from the puer, are washed in running water and placed in the pickle for an hour. The pickle consists of 8 pounds of salt, 2 pounds of aluminum sulphate and 1 pound of sulphuric acid having a specific gravity of 1.381. After pickling, the hides are dipped into a bath containing a chromium salt, one of which is made up by dissolving 10 pounds of sodium dichromate in 10 gallons of water; 6 pounds of syrup of glucose are added having a specific gravity of 1.381; 10 pounds of sulphuric acid are added, and the whole diluted to a specific gravity of 1.450. In using this solution 15 pounds are allowed for 100 pounds of pickled hides.

Formaldehyde is used in tanning to give a very light colored leather, that requires no bleaching. It resembles buff leather.

884. The Coloring Matter for Leather usually consists of coal tar dyes, such as nigrosine, for black. A solution of hematin in ammonium hydroxide may be used, followed by a striker of black iron and copper sulphate.

885. Cordite, a high explosive used in the war, has been found suitable for making artificial leather. A plant at Highland Park, Illinois, purchased 35,000,000 pounds of cordite from Great Britain to make artificial leather for the Ford Motor Company.

CHEMISTRY IN EVERYDAY LIFE

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CHAPTER XXXVII

SANITATION

While there are many practical problems of sanitation only a few of them can be touched upon in a single chapter. References to other parts of the book should be looked up by the student in order to review the topics mentioned.

886. Many of the Diseases Common to Mankind are caused by the multiplication of bacteria under conditions favorable for their growth. Such conditions can often be avoided by a little attention on the part of those whose duties include the care of grounds and outbuildings.

887. The Ash Pit is often used as a receptacle for garbage. When this is done it should be emptied twice a week at least. Where garbage is gathered separately from ashes, as in large towns and cities, it is often burned in large furnaces, fired with coal at first, until the heat developed is sufficient to raise the temperature to the combustion point. The smoke is burned by the use of smoke consumers and the clinker is used for road making or cement.

888. Outside Closets should be at least 6 feet from the house and 40 feet from the water supply. They should be constructed of brick, stone or cement to avoid saturation of the wood ordinarily used, and to make cleaning easier. They should be provided with removable buckets having covers to be used when they are emptied. Deodorants, such as wood ashes or lime should be used freely, or if these are not available dry earth may be substituted. Sulphuric acid is also a suitable substance since it changes the ammonia produced by the decay of the nitrogenous matter to ammonium sulphate.

889. Inside Water Closets should be provided with traps and should be thoroughly ventilated. The floor should be of

tile, or other non-absorbent material, and the walls should be tile or painted, not papered. These should not drain into a cess-pool since there is always danger of leakage and offensive odors, but they should drain directly from the house sewer into the main sewer.

890. Sewers should be of large diameter, and have no dead ends where the material can accumulate. There should be sufficient incline to cause a flow rapid enough to prevent clogging. Sewers are cleaned by flushing and are provided with openings for ventilation. Very frequently foul air comes from the sewers but the simultaneous discharge of potassium permanganate and sulphuric acid will usually overcome the smell, by oxidation.



Sewers usually carry storm water as well as sewage, so that in the rainy season the sewage may be very dilute. The amount of solid matter usually varies from 25 to 40 grains per gallon. Phosphoric acid, ammonia and potassium oxide are common components of sewage, and as the alkaline substances are in excess sewage is alkaline. The solid matter averages about 2 to 3 pounds per ton.

Dried sewage averages mineral matter, 49.8%; organic matter, 45.2%; nitrogen, 1.56%; fats, 3.44%. It has been estimated that the amount wasted per year is equal in fuel value to 44,000,000 tons of the best bituminous coal. The amount of manure wasted in 200 of the largest cities of the United States is estimated at 11,000,000 tons annually; while the waste from street sweepings in cities of over 1,000 is estimated at 5,000,000 tons annually, and the annual waste from shavings and sawdust is about 18,000,000 tons.

891. Purification of Sewage. Sewage may be purified by (1) allowing the solid matter to settle; (2) by chemical treatment; (3) by allowing the earth to absorb it; (4) by bacteria. The first method is not satisfactory. When *chemical treatment*

is applied various substances may be used. Lime alone applied as lime water makes the sewage more alkaline and hence more liable to putrefy. From 5 to 10 grains of aluminum sulphate, alum, or lime and alum, or 2 to 5 grains of ferrous sulphate per gallon will usually purify the sewage, but it has little value as a fertilizer after treatment. Magnesium chloride and lime mixture does not purify sewage sufficiently to allow it to flow into the streams. When sewage is purified by electrolysis, chlorine and oxygen are liberated at the positive pole, and form hypochlorous acid, which oxidizes the organic matter and forms iron hypochlorite; while at the negative pole, potassium oxide, sodium oxide, ammonia, magnesium oxide, etc. are formed and these decompose the iron hypochlorite. Hydrated ferrous oxide rises to the top as a scum mixed with air. It then passes to another tank where the impurities settle and the degree of purification is increased.

Where *land purification* is used the land should slope towards the south and be well drained. If the land is porous, one acre should be allowed per hundred tons of sewage, but if it is a clay soil one acre to 25 tons is the proportion. Various crops can be raised upon the land, such as Italian rye, grass, oziers, mangold, wurzel, and cabbage, but not cereals. The use of such vegetables, especially uncooked, leads to the development of intestinal parasites. This is common among the Chinese.

892. Septic Tanks for the purification of sewage depend upon the action of anaerobic organisms (that is, organisms able to live without air which grow in the tanks) upon the bacteria, with which the sewage is filled. Chemical changes occur and the more complicated compounds break down into simpler compounds—liquid and solid organic compounds, and some mineral compounds, so slight that the tanks are seldom cleaned. The top of the tank is covered with a scum, from 2 to 12 inches thick, and the organic matter is changed into ammonia, carbon dioxide, water, hydrogen, methane, carbon monoxide, nitrates, nitrites, etc. If the tanks are covered the

gases accumulate and may be used for fuel or lighting. The flow of the sewage through the tanks is very slow, requiring 12 to 24 hours. The sewage then flows over coke filtering beds from 4 to 13 feet thick consisting of lumps of coke from $1/2$ to 2 inches in diameter, resting upon perforated tiles. More of the anaërobic organisms develop on the coke, but the beds are not ready for use until after about four weeks, after which they will last for years. The filter beds should be used in rotation. Typhoid bacilli are killed in 4 days, and cholera spirilli in 3 days.

893. Activated Sludge furnishes the latest method of purifying sewage. This method does not depend upon the action of chemicals added to the sewage, but upon the action of metabolic chemicals liberated in the sewage itself by the action of bacteria.

Raw sewage is placed in a tank 18 feet high and 12 feet in diameter. Air is bubbled through, and the heavier particles, known as sludge, settle to the bottom. The water is drawn off and more sewage is added and the process repeated until at last the sludge becomes active and nitrification takes place in a very short time. The activating process is at first slow, requiring nearly 5 weeks for the first sewage, 15 days for the second, 4 days for the third, gradually reducing to 4 hours for the thirty-first. After the process has been started it may be said to require on an average about 10 hours for nitrification. The residue is sold as a fertilizer, and has a market value of from \$4.00 to \$5.00 a ton.

894. Disposal of the Dead. It requires about 14 years for the complete decomposition of the buried body of an adult and about 8 years for a child. These times may be lengthened or shortened according to the style of coffin. On the other hand cremation reduces the body to about 3 pounds of incombustible ash in 2 hours, and avoids any possibility of contagion.

895. Disinfectants. A disinfectant is a substance that will kill organisms that act injuriously upon higher forms of life.

Disinfectants are usually antiseptics and deodorants as well as germicides. An antiseptic may merely retard the growth and not kill. Disinfectants may not kill all the organisms but may leave a residue that is highly resistant. The general chemical description of the disinfectants mentioned here may be found in the parts of the text referred to.

Oxygen acts slowly as a disinfectant, by the aid of anaerobic organisms, but faster if compressed. *Ozone*, an allotropic modification of oxygen, is exceedingly energetic when moist, but inactive when dry. Ozone is used both for the purification of water and air, but in the latter case the action is slow and in order to be very effective the amount required will produce an irritant action upon the lungs. See Chapter 2.

Hydrogen Dioxide when added in the proportion of 0.6 gram per liter and kept at a temperature of 52° to 55° for 8 hours will keep milk sweet for a month. Hydrogen dioxide is sold under many other names, as hydrogen peroxide, dioxygen, each usually 3%; perhydrol, 30%; hydrozone, glycozone, pyrozone, etc. It is found in sanitas, while corresponding metallic compounds are known as peroxides, among which are sodium peroxide (oxone); magnesium peroxide (heptogan); zinc peroxide (ektogan) etc.

Nitric Acid and the oxides of nitrogen, as nitrogen tetroxide, are powerful disinfectants, but are very costly and dangerous when compared with others.

Sulphur is used in various ways, chiefly in its compounds. The dry powder may be used for insects and fungi on plants, or it may be used as calcium polysulphide, made by boiling milk of lime with sulphur. *Sulphur dioxide* generally does not kill spores, and the dry gas has but little effect upon micro-organisms, but it destroys vermin. Sulphur dioxide is suffocating, and as little as 5% in the air has been known to prove fatal. It has little penetrating power and requires 16 to 24 hours to be effective with vermin. It may be prepared by burning sulphur in the air or by exposing liquid sulphur dioxide to the air.

Sulphur dioxide and the metallic bisulphites check fermentations and are used to preserve foods. *Sulphuric acid* is a powerful disinfectant, 0.04% killing cholera germs in sewage. When water has ordinary typhoid infection the bacilli may be killed in 30 minutes with 0.035% H_2SO_4 , or in 15 minutes with 0.07%. As the sodium salt, sodium bisulphate, NaHSO_4 , 15 grains to the pint will kill in 15 minutes typhoid and cholera germs and will destroy intestinal parasitic worms. *Carbon disulphide*, CS_2 , is used for destroying fungi and insect parasites, as vine phylloxera. It is also used with success for destroying prairie dogs, ants, etc.

Boric Acid, H_3BO_3 , is not a disinfectant, but restrains the growth of bacteria in foods. When a boric mixture, consisting of 3 parts of boric acid and 1 part of borax is used, 1 part in 2,000 will keep milk sweet for 24 hours without acting injuriously upon the digestive system.

The Halogens, chlorine, bromine and iodine—act in three ways (1) they can combine with the hydrogen, thereby liberating oxygen in water; (2) they can combine directly with organic matter; (3) they can replace hydrogen in organic matter and precipitate albuminous substances, killing organisms by combining with and coagulating the protoplasm, by removing the food, or by acting as an irritant or a direct poison. Free chlorine is usually not used, because of the difficulty of handling it so that various compounds are used instead, such as the hypochlorites, the most common being calcium hypochlorite, $\text{Ca}(\text{ClO})_2$ which is nearly 50% chlorine. When exposed to moist air it deliquesces and is gradually decomposed, acting upon less resistant organisms in about 24 hours. Sodium hypochlorite, NaClO , is used as *Eau de Labarraque*, or as *Eau de Javelle* (which originally used potassium hypochlorite). In these waters is about $2\frac{1}{2}\%$ of available chlorine. *Anti-formin* is a solution of sodium hydroxide and sodium hypochlorite. Calcium hypochlorite increases the hardness of water and gives a bitter taste, while sodium hypochlorite softens

it and gives no taste. One part of available chlorine in from 1 to 8 million parts of water is usually sufficient for purifying drinking water, and produces no bad effects upon the system. In 1920 the death rate from typhoid in Chicago was reduced through the use of chlorine in the drinking water to 1.1 per 100,000, the lowest rate for any large city. Much more is required for the purification of sewage, usually from 30 to 70 parts of chlorine per million. Sodium hypochlorite is used for the purification of the water in swimming pools, destroying the surface growths of algae and fungi which often harbor dangerous organisms. *Ferrochlor* is a mixture of 8 parts of ferric chloride and 0.5 part calcium hypochlorite. *Bromine* in the form of potassium bromide, KBr, is sometimes used in the proportion of 40 to 60 parts per million, but it is bulky and the use of bromine is dangerous. *Iodine* acts as a germicide and 1% dissolved in alcohol is used to wash the skin before operations or the use of the hypodermic needle.

Acids are generally unfavorable for the growth of bacteria and typhoid bacilli in a broth or gelatin preparation may be prevented from growing by 0.08% H_2SO_4 , 0.2% HCl, or HNO_3 ; 0.28% SO_2 ; 0.31 to 0.4% phosphoric, acetic, carbolic, formic, oxalic or lactic acid; 0.476% tartaric, citric or malic acid; 1.66% tannic acid; or 2.7% boric acid. Hydrochloric acid is effective against cholera, while anthrax may be overcome by hydrochloric, hydrofluoric, sulphuric, nitric, hydrobromic or chloric acid.

Dry Lime is fatal to bacteria, but it is not entirely safe to rely upon it for burying infected bodies unless a long time elapses before the body is removed, since live germs may be diffused.

Potassium permanganate is a good disinfectant for wells, cisterns, etc. Enough of the permanganate should be added to produce a pink color for 24 hours. The color and odor of the water are both removed by the process of oxidation. (See §528). Usually about two ounces are sufficient for an ordinary cistern.

Arsenic trioxide is more effective upon higher forms of life than it is upon the lower forms, and therefore is not considered a good disinfectant.

Of the Copper Salts, cuprous chloride, CuCl , is considered the most effective. When water is treated with 50 parts of cuprous chloride and 20 parts of ferrous sulphate per million and allowed to stand 6 hours and then treated with 10 parts of lime, the water after settling will be free from iron and copper, thoroughly sterilized and free from color and odor. For agricultural purposes copper sulphate is used against potato blight, and for soaking seeds. Verdigris (acetate), Paris green (arsenite), copper-lime-sugar, and copper-soap washes are used for trees; and Bordeaux mixture, copper sulphate and lime, is used on vines. A suitable Bordeaux mixture consists of 3 pounds of copper sulphate and 2 pounds of fresh calcium oxide to 10 gallons of water.

Mercuric Chloride, HgCl_2 , is one of the most powerful disinfectants. The early standard was 1 part in 1,000. It is costly, poisonous to higher animals and to plants and is easily precipitated. If $\frac{1}{2}$ ounce of mercuric chloride is dissolved in 3 gallons of water, with the addition of $\frac{1}{2}$ ounce of hydrochloric acid, and about 5 grams of an aniline dye, as a safety color, the strength is 1 part in 962. The germicidal power of mercuric chloride depends upon the degree of ionization, so that 1 part in 500 is much less than twice as active as 1 part in 1,000.

Silver Nitrate, AgNO_3 , stands next to mercuric chloride, but has similar limitations. To avoid irritant action and precipitation by chlorides a large number of organic compounds of silver have recently been introduced, such as argonine (with casein); argyrol (with gluten); largin (with albumen); protargol (with protein); etc.

Formaldehyde, CH_2O , is usually used in the 40% solution, sold as formalin. When 1 part of formaldehyde is added to 50,000 parts of milk, or 1 part of formalin to 20,000 parts of milk, the milk will keep sweet for 24 hours. It is however,

illegal to use it in that manner. Fruit, left in a solution of 3 pints of formalin in 10 gallons of water, will keep for 10 to 21 days longer without spoiling. Formalin, diluted to 10 volumes, is used for embalming. A $1\frac{1}{2}\%$ solution is sometimes effective in eczema. Wood smoke, used for preserving meats, contains 1 part of formaldehyde in 10,000 to 100,000. It is also found in tobacco smoke. Formaldehyde can be easily applied either as a gas or as a liquid or in the solid form as polymers. It is not rendered inactive by albuminous matter or most chemicals, and is effective in strengths that are not irritative or poisonous. One polymer of formaldehyde, known as *paraform*, dissociates into formaldehyde when heated. The amount required to be effective against diphtheria, typhoid and moist anthrax is 10 grams per 1,000 cubic feet, the action continuing for 20 to 24 hours. The action is better if the walls of the room are sprayed with water first or if water is vaporized at the same time. The residual formaldehyde can be neutralized by volatilizing ammonia, forming solid, inodorous, hexamethylenetetramine, $C_6H_{12}N_4$, which is sold under the trade name of Urotropin. This is given to typhoid convalescents or others to kill the bacteria which for a long time continue to be discharged in the urine.

Acetic acid, $HC_2H_3O_2$, the acid of vinegar, is one of the old preservatives. Pyroligneous acid or crude wood vinegar, owes its power to the presence of creosote and formaldehyde.

Citric, Tartaric and Malic Acids have the power to stop the growth of bacteria that prefer a neutral to an acid medium, but their effect is much less than that of the mineral acids, while they cost more, and the solutions become mouldy in warm weather.

Benzoic Acid and its salts are strongly antiseptic. The acid is stronger than its salts, 0.022% retarding souring, while with sodium benzoate, 0.026%, and with potassium benzoate, 0.029%, is required.

Salicylic Acid acts in about the same manner and about as effectively as benzoic acid. It produces no marked injury to adults when used in limited amounts. Salol is phenyl salicylate and decomposes in the duodenum into phenol and salicylic acid. Sodium salicylate or sodium benzoate are often administered in the early stages of appendicitis. They act by stopping the fermentation, and when accompanied by other treatment will usually stop the distress in 24 hours or less.

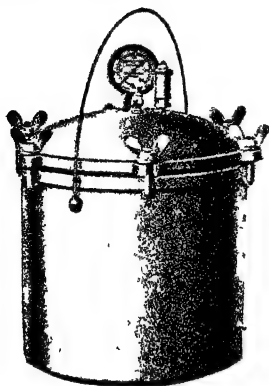


FIG. 207 A Sterilizer for Family Use

896. Sterilization by Heat. A small sterilizer, which may also be used as a pressure cooker, (see Fig. 207) may be purchased at a moderate cost. Canned fruit, cooking utensils, etc., may be sterilized by placing the article in the sterilizer, adding water, fastening the lid, and heating until the steam gage registers from 20 to 30 pounds.

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CHAPTER XXXVIII

MEDICINES AND PATENT MEDICINES

Only a few of the more common substances used in medicines can be described in a single chapter. These will be grouped according to their effect, rather than upon their chemical composition.

897. Disinfectants. See §895 etc. Many commonly used disinfectants are described elsewhere throughout the text. Among these are boric acid, benzoic acid, salicylic acid, silver nitrate, mercuric chloride, potassium permanganate, hydrogen peroxide, iodine, iodoform, sulphur, phenol, etc. A new disinfectant, known as *Dakin's solution* was produced during the World War. This has since been modified and now is manufactured under the trade name of "Chlorazene." Its chemical name is para-toluene-sodium-sulphochloramide. It is marketed in 4.6 grain tablets, the recommended strength of the solution to be used being 1 tablet in one ounce of water, which gives approximately a 1% solution. The tablets are nearly odorless, but the solution gives a faint odor of chlorine. The solution is nontoxic and noncaustic. It is intended for external use only, but has been used as a mouth and throat disinfectant although the solution should never be swallowed.

898. Corrosives and Caustics, applied for the purpose of destroying tissue, include such substances as acetic acid, nitric acid, dehydrated alum, silver nitrate, arsenic trioxide, chromium trioxide, iodine, phenol, potassium carbonate, potassium hydroxide, sodium carbonate, sodium hydroxide and zinc chloride, all of which have been described elsewhere in the text. Consult index for section references.

899. Astringents have the power to cause contraction and include tannic acid, alum, barium chloride, silver nitrate, bismuth subcarbonate, bismuth subnitrate, copper sulphate,

ferric chloride, ferrous sulphate, lead acetate, zinc oxide and zinc sulphate. Some of these are used to stop bleeding.

900. Powders for dusting over parts of the body, or for face powders, include various forms of starch, bismuth subcarbonate, bismuth subnitrate, magnesium carbonate, precipitated chalk (calcium carbonate), rice powder, kaolin, talcum, zinc oxide, and some of the stearates, oleates, etc., such as zinc stearate and zinc oleate.

901. Protectives, either to keep the air from a bruised or burned surface or as used in various cold creams, so-called flesh foods, etc., include the various fixed oils and fats, which are neutral esters of vegetable or animal origin, and are compounds of glycerol with acids, chiefly oleic, palmitic and stearic; lard, lanolin or wool fat, beeswax, petrolatum which is sold under many different names, such as vaseline, litholine, etc., ceresine or mineral wax, spermacetti from the sperm whale, etc. Most of these turn rancid on standing. For use they are either applied alone or in various mixtures, melted at a low temperature, and mixed with white mineral oil, perfume, etc., so as to make them easy and pleasant to apply.

902. Anesthetics are divided into two classes, general and local. General anesthetics include nitrogen monoxide (see §139), chloroform, ether, or mixtures of alcohol, chloroform and ether.

Chloroform, CHCl_3 , or trichlormethane, may be prepared by the action of bleaching powder upon alcohol or acetone. It is a colorless, heavy liquid with a sweetish taste. Its specific gravity is 1.52637. It boils at 61.2° and does not solidify except below -70° . Pure chloroform decomposes slowly, but is made more stable by the addition of about 1% of alcohol. Chloroform is widely used as an anesthetic. The use of chloroform as a general anesthetic is considered to be more dangerous than the use of ether, or a mixture of alcohol, ether and chloroform.

Ether, $(\text{C}_2\text{H}_5)_2\text{O}$, or ethyl oxide, is often called sulphuric ether, from the method of manufacture, and not because of the

presence of the sulphate radical. It is made by distilling a mixture of 200 parts of alcohol and 360 parts of concentrated sulphuric acid by weight, so that the mixture distils over at 140° . Ether, mixed with alcohol and water, distils over and if alcohol is run into the distilling flask at a rate to keep the temperature constant the process is continuous. If water is added to the distillate the ether will rise to the top and may be separated by a pipette or separatory funnel after which it should be treated with a little calcium chloride and distilled on a water-bath. When pure it boils at 34.6° . Its specific gravity is 0.736 at 0° and 0.718 at 15.6° . It dissolves in 11.1 volumes of water at 25° , and will dissolve $1/50$ its volume of water. Ether is very inflammable and should never be heated over a free flame, but over a water-bath in which the temperature is below the boiling point. It vaporizes rapidly and forms explosive mixtures with air. Commercial ether usually contains alcohol. Ether mixes with alcohol in all proportions. It is used as a solvent for fats, resins, alkaloids, etc., as an anesthetic, and on account of its rapid evaporation is used to produce lower temperatures. When heated with water and a small amount of sulphuric acid it is converted into ethyl alcohol.

Local Anesthetics are applied to a small area to produce local insensibility to pain. Among these are cocaine, codeine, stovaine, menthol, etc. Sometimes freezing is produced by a spray of ethyl chloride or by solid carbon dioxide, often called carbon dioxide snow.

Ethyl Chloride is a colorless, very volatile liquid, having an agreeable odor, and a sweetish, burning taste. It is kept in hermetically sealed tubes, in a cool dark place. It is used in the form of a spray as a local anesthetic for minor operations. It will produce general anesthesia if inhaled but is dangerous, acting after the general manner of chloroform. When applied as a local anesthetic in the form of a spray the surface upon which the spray falls may be frozen.

Cocaine, $C_{17}H_{21}NO_4$, is an alkaloid obtained from several varieties of Coca. It forms large colorless prisms, having a slightly bitter taste, and producing on the tongue a temporary numbness. When applied locally, cocaine paralyzes the peripheral nerves, causing loss of sensation, and contracts the blood vessels. When injected into a nerve, or around a nerve sheath, local anesthesia is produced.

Coderne is an alkaloid obtained from opium, or prepared from morphine by methylation. It occurs as white nearly translucent crystals or as a crystalline powder, odorless and having a slightly bitter taste. During recent years it has come to be used widely in place of morphine. It is also used as the hydrochloride, nitrate, phosphate, sulphate, etc.

Stovaine is closely related to alypin. It is a local anesthetic having about the same power as cocaine but dilates instead of contracting the blood vessels. It is $\frac{1}{3}$ to $\frac{1}{2}$ as toxic as cocaine, and is said to act as a heart tonic.

Alypin, like stovaine, is an amino-benzoic acid compound. It is less toxic than cocaine but has about the same power.

Menthol is a secondary alcohol obtained from oil of peppermint, closely allied to camphor, $C_{10}H_{16}O$, obtained by distilling camphor wood chips in water. Menthol occurs as colorless prismatic crystals, having a strong and pure odor of peppermint, and a warm aromatic taste, followed by a sensation of cold when a stream of air is drawn into the mouth. It is used both internally and externally, for the latter purpose often in the form of pencils that are rubbed over the painful part as in the relief of neuralgia or headache and in ointments. It is also used extensively as an inhaler, the menthol being placed in a glass tube, contracted at one end, so that the air taken into the nose is drawn through the menthol.

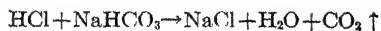
903. Emetics are used to cause vomiting, and usually act by causing local irritation. Ipecac, mustard, sodium chloride, zinc sulphate, and many other substances will produce the desired result. Some people vomit after a dose of magnesium

sulphate, or from smelling tincture of ferric chloride. Ipecac is not very trustworthy. When mustard is used the ground seed of the black mustard is given, about $\frac{1}{4}$ ounce being sufficient. When warm sodium chloride is used from 2 to 3 pints may be necessary.

Anti-emetics act by lessening irritation and vomiting, by exerting a depressant effect. Among these are bismuth subcarbonate, bismuth subnitrate, chloral hydrate, chloroform, cocaine, codeine, menthol, morphine and opium.

Chloral Hydrate, $\text{CCl}_3\text{CH}(\text{OH})_2$, occurs as transparent, colorless crystals, having an aromatic penetrating odor, and a bitterish, caustic taste. It is very soluble in water, alcohol, and ether. Chloral hydrate acts upon the central nervous system, producing a feeling of weariness, followed by quiet sleep, in which the pulse and respiration are slowed in the same manner as in normal sleep, and the reflexes are not abolished. From the sleep the person can be readily awakened. Fatal doses cause death by paralysis of the respiratory center or paralysis of a weakened heart. Large doses are dangerous, and it should never be taken except under the advice of a physician.

904. Antacids, to lessen the acidity of the stomach, are naturally alkaline in their nature. Calcium carbonate, chalk, magnesium carbonate, magnesium oxide, potassium carbonate, sodium bicarbonate, and sodium hydroxide are the more commonly used substances. Sodium bicarbonate is ordinary baking soda, and may be used in solution as an antacid, or as commonly said "to sweeten a sour stomach." The more expensive soda mint tablets, used widely, are made of sodium bicarbonate flavored with a little oil of peppermint. The hydrochloric acid of the stomach reacts with the sodium bicarbonate



905. Purgatives. Owing largely to overeating, and lack of sufficient exercise, many people have more or less trouble from constipation. There are several classes of purgatives, among

which the vegetable, saline and mercurial purgatives are the most commonly used.

Vegetable purgatives are quite numerous, the most widely used being *castor oil*. The disagreeable taste of castor oil may be overcome by the addition of saccharin and oil of peppermint.

Cascara Sagrada is the dried bark of *Rhamnus Purshiana*. It is most agreeably used as the aromatic fluidextract. In this form the bitter principle has been removed and the taste improved by the addition of licorice and compound spirit of orange. As a laxative it acts mainly on the colon and is widely used for habitual constipation. The dose is about 2cc. at bedtime, and can be gradually reduced without causing constipation.

Rhubarb, used as the dried powder, the extract, or the aromatic tincture, acts chiefly on the colon and has the tendency to produce constipation after the initial laxative effect. Rhubarb preparations are, therefore, appropriate remedies at the beginning of diarrhea, since they cause the expulsion of irritating substances and promote a return to normal by their constipating influence.

Senna belongs to the anthraquinone-containing group of vegetable purgatives and is considered to be one of the most efficient drugs of this class. It is largely used for the treatment of chronic constipation. It is often mixed with figs and dates before taking.

Among the Saline Purgatives are magnesium sulphate, known as Epsom salt, magnesium carbonate, magnesium oxide and magnesium citrate. The last is usually taken in the form of Liquor magnesium citrate, made by mixing magnesium carbonate, sodium or potassium bicarbonate, citric acid and sugar in a strong bottle properly stoppered. The bicarbonate should be added last. When the bottle is opened the carbon dioxide escapes from pressure and the liquid carries a copious foam. The taste resembles lemonade. Other saline purgatives are potassium bitartrate, potassium citrate, potassium sodium

tartrate, sodium chloride, sodium phosphate and sodium sulphate.

Mercurous Chloride or calomel, is not irritating, but produces laxative effects by slow action. Minute doses are generally effective, but all things considered, it is better to use other, safer and pleasanter remedies.

906. Chemicals that Affect the Urinary System. Chemicals that *increase the flow of the urine* are known as diuretics. Among them are spirits of nitrous ether, caffeine, cubebs, mercurous chloride, potassium acetate, potassium citrate, potassium nitrate, sodium nitrite and theobromine. Others that *render the urine less acid* and thus diminish burning sensations, when there is too much acid in the urine, are potassium acetate, potassium bicarbonate, potassium citrate, sodium bicarbonate, and sodium carbonate. Acid urine is more antiseptic than alkaline and in order to *make the urine more acid* sodium acid phosphate or mineral acids are prescribed. Other agents to *make the urine antiseptic* are benzoic acid, salicylic acid, aspirin, hexamethylenamine, commonly called urotropin or formin, phenyl salicylate, sodium benzoate, sodium borate, sodium salicylate besides local antiseptics.

907. The Action of the Respiratory System may be quickened by the use of atropine, caffeine, camphor, or strychnine. *Irritability in the cough center* is reduced by chloral hydrate, chloroform, codeine, morphine and opium. The *secretions of the bronchial tubes are increased and liquefied* by the use of ammonium chloride, ammonium and potassium tartrate, apomorphine hydrochloride, ipecac, potassium iodide, and sodium iodide. Bronchial spasm in asthma is relaxed by atropine, belladonna, sodium iodide, sodium nitrite.

Apomorphine hydrochloride is the hydrochloride of an artificial alkaloid prepared from morphine by the abstraction of one molecule of water. It is used chiefly as an emetic and acts directly upon the vomiting center independently of a local action on the stomach. It produces a prompt emptying of the stomach

with little subsequent sickness unless the dose is large. It is often used also as an emetic in poisoning when the stomach tube cannot be used.

908. The Central Nervous System is Stimulated by the use of strychnine for the spinal cord; or atropine, caffeine or camphor for the brain and medulla. *General anesthetics* for paralyzing sensation are ether, chloroform, ethyl chloride and nitrous oxide. *Hypnotics or narcotics to induce sleep or rest* are alcohol, chloral hydrate, codeine, morphine, opium, paraldehyde, etc. *Analgesics or Anodynes* are used to *relieve pain*, and include acetanilid, acetphenetidin, salicylic acid, alcohol, antipyrine, aspirin, chloral hydrate, codeine, methyl salicylate, morphine, and sodium salicylate. *Drugs used to reduce the temperature in fevers* include acetanilid, acetphenetidin, salicylic acid, aconite, ammonium acetate, antipyrine, aspirin, guaiacol (from beechwood creosote) phenol, quinine and sodium salicylate.

909. The Blood Is Affected by the Use of Chemicals in several ways. To *increase the hemoglobin* arsenic trioxide, various compounds of iron such as the carbonate, iodide, phosphate, and the citrate of iron and ammonium are among the most commonly used. The *blood is rendered alkaline* by the use of the same substances used for rendering the urine alkaline, and sodium hydroxide is also used.

910. Among the Many Substances Used for Overcoming Parasitic Skin Diseases are balsam of Peru, benzoin, camphor, menthol, chrysorobin, mercury, ichthyol, iodine, tar, resorcinol, sulphur, thymol, oil of cade, beta naphthol, etc. These are usually made up into ointments with lard, vaseline, lanum, or other greasy base and applied to the affected parts at night.

911. Substances Acting on the Eye otherwise than as an antiseptic wash are (1) mydriatics, which dilate the pupil and increase the accommodation such as atropine, cocaine, homatropine hydrobromide, and scopolamine hydrobromide; (2) myotics, which contract the pupil and the ciliary muscles such as

physostigmine salicylate, also called eserine salicylate, derived from the calabar bean, and pilocarpine hydrochloride, derived from jaborandi.

912. Administering of Medicines. Many substances are administered in *solution form* but this is often impossible, or undesirable on account of the taste. The more common methods of administering are the following:

Cachets or wafers where a mixture of flour, starch, water and the powdered drug is pressed between hot iron plates. They are more readily dissolved than capsules and are easily swallowed if previously dipped into water.

Capsules are either hard or soft. They are made of gelatin or gelatin and glycerol in different shapes and sizes for administering powders, oils, and various liquids.

Cataplasms or poultices are soft solid preparations used for applying heat and moisture to localized areas of the body. They may contain counter irritant drugs. A long continued application of a poultice tends to cause relaxation of the skin and to render it flabby.

Cerates are mixtures of fats and waxes with medicinal agents softening and adhering to the skin to which they may be applied by spreading the cerate on cloth or paper.

Chartae or medicated papers are pieces of absorbent paper that have been treated with medicinal substances, or sized paper that has been coated with a layer of the medicinal substance.

Collodia or collodions are alcohol-ether solutions of collodion cotton, (pyroxylin) with or without medicinal agents. Flexible collodion is ordinary collodion with 5% Canada turpentine (Canada balsam) and 3% castor oil. The castor oil makes the film more tenacious and flexible. The turpentine is unnecessary. Iodine, iodoform, salicylic acid, etc. are often added for special purposes.

Confections, conserves, or electuaries, formerly used to a large extent, are soft, pasty masses of honey or sugar, containing the active drugs and often flavoring substances.

Decoctions are water solutions made by boiling the substance in water and then straining.

Elixirs are sweetened, aromatic, agreeably flavored alcoholic liquids, similar to cordials, and serve either as vehicles to disguise the taste of bitter or nauseous drugs, or they may contain medicinal agents.

Emplastra or Plasters are solid preparations for external use, and serve either as simple adhesives or as counter irritants. Most adhesive plasters are made from lead plaster, made pliable with rubber and petrolatum, in which the medicinal agents are mixed.

Emulsions are aqueous preparations in which oils, resins, fatty, or other insoluble substances are held in suspension by the use of gum, mucilage or other emulsifying agents. Milk is a natural emulsion.

Enemata, or Clysters are liquid preparations intended to be injected into the rectum to overcome constipation.

Essential Oils, see *Olea Volatilia*.

Extracts are soft solid, or powdered, preparations, made by evaporating the soluble principles of drugs that have been extracted by the use of water, alcohol, or some other solvent. The evaporation is carried to the point where the material forms a soft solid, or until it may be reduced to a powder, either with or without the addition of a diluent, such as milk sugar, or powdered licorice. The average strength of extracts is about four times the strength of the raw materials and hence the dose is usually $\frac{1}{4}$ that of the crude drug.

Fixed Oils, see *Olea Pingua*.

Fluidextracts are liquid preparations of uniform and definite strength, so that 1 cc. represents the soluble ingredients of 1 gram of the crude drug.

Glycerites are solutions of medicinal substances in glycerol.

Honeys, see *Mellita*.

Infusions are usually made by taking 5 grams of the cut or bruised drug, over which is poured sufficient boiling water to

make 100 cc. This should be done in a non-metallic vessel and the vessel is covered. After standing for one-half hour in a warm place it is pressed and water is added to make up the required amount. Infusions should not be made from fluid extracts.

Liniments are solutions of medicinal substances in alcohol, oil or liquid soap, for external application.

Liquores or *Solutions* are usually solutions of chemical salts in water. Chlorine water and formalin are, however, classed with solutions.

Lozenges, see *Troches*.

Masses are soft, solid preparations of such consistency that they can be made into pills readily.

Mellita or *Honeys* are sweet liquids having honey as a base, but are not used as much as in former times.

Misturae or *Mixtures* are liquid preparations containing partly soluble or insoluble substances suspended in them, often with sugar, mucilage, etc. They are usually unstable, and should be prepared as needed.

Mucilages are liquid extracts of mucilaginous drugs or solutions of gum in water, such as gum arabic. They are often used as an addition to mixtures for internal use or as an emollient and lubricant in mixtures for external use.

Ointments, see *Unguenta*.

Oleates are solutions of alkaloids or metallic oxides in oleic acid. They are of liquid or semi-solid consistence and are intended for external use. In some of the oleates half of the oleic acid is replaced by olive oil.

Olea Pingua or *Fixed Oils* are the natural esters of vegetable or animal derivation, and chemically are salts or compounds of an acid, such as oleic, palmitic, or stearic with the glyceryl radical. Alkalies act upon them to form soaps. The glycerol is set free. Oils are insoluble in water, but are often found in emulsions.

Olea Volatilia, or *Volatile (Essential) Oils* are derived from plants and may contain, or consist of, neutral principles,

aldehydes, ketones, phenols, and esters, or compound ethers. They are mostly insoluble in water but are soluble in alcohol and are used as extracts and for flavoring.

Oleo-resins are thick liquid preparations consisting of volatile oils and resins, extracted from vegetable substances by ether, acetone or alcohol.

Paste Pencils, see *Stili Dilubiles*

Pilulae or *Pills* are round, oval or flattened bodies of medicinal substances combined with other material and weigh between 0.06 and 0.5 gram. If weighing between 0.02 and 0.06 gram they are known as *granules* and if less than 0.02 gram they are called *parvules*. They may be covered with dusting powder if made fresh; but if they are to be kept for some time, or if it is desirable to mask the taste, they are covered with some substance that dissolves readily in the juices of the stomach, such as sugar, gelatin or chocolate. Sometimes it is necessary to cover the pills with a substance that will not dissolve in the acid juices of the stomach but which will dissolve in the alkaline juices of the intestines. In such cases salol, keratin, etc., are used.

Plasters, see *Emplastra*.

Poultices, see *Cataplasms*.

Powders are either powdered medicinal drugs, or a combination of two or more medicinal substances, either with or without a diluent, such as milk sugar. The term is also applied to single doses of powdered substances wrapped separately in powder papers.

Salts, Effervescent, are mixtures of soluble salts with sodium bicarbonate and citric acid, or tartaric acid, or both. When put into water, carbon dioxide is set free and makes an effervescing drink.

Serums, Viruses and Vaccines are special preparations not conforming to the same standards, but treated separately, and are particularly tested for freedom from bacterial and toxic contamination. Antidiphtheric serum or diphtheria antitoxin

is a fluid separated from the coagulated blood of the horse immunized through the inoculation of diphtheria toxin. Antitetanic serum is the blood serum of horses immunized to the toxin of the tetanus bacillus. Vaccine virus is the material obtained from skin eruptions of calves having vaccinia. The pulp is ground and mixed with varying percentages of glycerol. It is usually marketed in capillary tubes or as glycerinated points.

Solutions, see *Liquores*.

Spirits are alcoholic solutions of volatile substances, either gaseous, liquid or solid. A number of the spirits are solutions of the volatile oils, and are used chiefly as flavors, stimulants and tonics.

Stili Dilubiles, or *Paste Pencils*, also known as Unna pencils, have the medicinal agent incorporated with a paste consisting of starch, dextrin, tragacanth and sugar, with sufficient water to form a plastic mass. This is rolled into cylinders having a diameter of about 5 mm. and the cylinders are cut into sections about 5 cm. long, dried on parchment paper at room temperature and wrapped in tinfoil. Salicylic acid 10%, or cocaine 5% are examples of the medicinal agents thus used. The pencils are applied directly to the skin.

Suppositories consist of a medicinal substance incorporated with a carrying vehicle that melts quickly when introduced into any of the natural openings of the body for which they are intended. The usual vehicle is oil of theobroma, commonly called cocoa butter, but may be soap, glycerine or glycerinated gelatin for certain purposes. The medicinal agent should be evenly distributed throughout the suppository by very thorough mixing. The mixture is melted and poured into chilled molds, or made into an ointment-like mass and pressed into molds by means of a screw press.

Syrups are very nearly saturated solutions of sugar in water, with or without the addition of medicinal agents.

Tablets are made by mixing the medicinal agent with pow-

dered milk sugar or powdered sugar, moistening with sufficient alcohol to make a paste and pressing into suitable molds.

Tinctures are usually extractive preparations of vegetable drugs, made with alcohol or with alcohol and water. When potent drugs are used 100 cc. represents the active principle of 10 grams of the drug; with the less potent drugs 100 cc. may contain the active principle of 20 grams.

Triturations are mixtures of medicinal substances with an inert diluent, such as milk sugar. Usually 10 grams of the medicinal substance is incorporated with 90 grams of milk sugar. Triturations are particularly adapted to insoluble or sparingly soluble substances intended for internal administration, and make a very accurate method of dispensing small quantities of active drugs.

Troches or Lozenges have the medicinal substance made into a soft paste or confection, which is divided into doses and dried. They are used chiefly for administering astringent, antacid, or antiseptic drugs that are intended to act upon the mouth and throat, and are administered by allowing the troche to dissolve upon the tongue slowly, thus permitting the medicinal substance to come in contact with the affected parts.

Unguenta or Ointments are semisolid mixtures of fats and oils, sometimes with wax, lanolin, petrolatum, etc., with which the medicinal agents are intimately incorporated. They are rubbed upon the body, and hence the vehicles used should melt at the temperature of the body. The choice of the oil or fat to be used is dependent upon the action desired. Petrolatum does not penetrate the skin, while lanolin penetrates so readily that the medicinal substances are taken through the skin and such substances as iodine, mercury, etc., may be absorbed in the system. The vegetable and animal fats and oils stand between these two and penetrate into the skin, but not through it. Vegetable and animal fats and oils easily become rancid and are also affected by many of the chemical reagents, a mixture of

equal parts of petrolatum and lanolin is about as favorable a medium for most substances as can be desired.

Careful analysis shows that the best made ointments are not homogeneous even when first made and consequently cannot be so after standing, especially since changes are apt to occur in some of them.



FIG. 208. A Bottle of Chemically Pure Sodium Oxalate, Showing Purity on the Label.

Vaccines, see Serums.

Vina, or *Medicated Wines* are solutions of medicinal substances in wine, usually white wine since it contains less tannin. The wine is usually sweetened and strengthened with alcohol. Because of the great variation in the wines, and the unsatisfactory results obtained when it is used as an extractive, the use of medicated wines is on the decline.

913. Quality. All substances taken as medicine should have the highest degree of purity. These are designated as U. S. P. (according to the United States Pharmacopeia) or C. P. (chemically pure). Fig. 208 shows a bottle of C. P. sodium oxalate with the maximum amount of impurities indicated. It is practically impossible, and usually unnecessary, to obtain absolute purity, but the impurities should always be known. The following label shows a typical analysis of a C. P. chemical.

COBALT CHLORIDE C. P. Maximum Limits of Impurities

Sulphates (SO_3)	0.0100%
Alkali Salts	0.2500%
Zinc (Zn)	0.0800%
Lead (Pb)	0.0200%
Copper (Cu)	0.0020%
Nickel (Ni)	0.1000%

PATENT MEDICINES

914. "Patent" and Proprietary Medicines Defined. A patent medicine, in the legal sense of the term, is a medicine whose composition, or method of making, or both, have been patented. It is not a secret preparation, because its composition must appear in the specifications at Washington. Moreover, a patent medicine becomes public property at the end of seventeen years, since at that time the patent expires. Strictly speaking, there are very few patented medicines on the market, and the term is generally applied to what are more properly called "proprietary" medicines. These concoctions are given fanciful names, and the names, after registration at Washington, become the property of the owner for all time. The composition of the preparation and the curative effects claimed for it may be changed as often as desired, but the proprietorship of the name remains unchanged. In the ordinary meaning of the words, however, it is customary for people to apply the term "patent" medicine to all medicines made and sold by any manufacturer through druggists or direct to the consumer, where the physician has not given a special prescription. In this chapter the term "patent" medicine will be used in the ordinary meaning of the word, not in the strict legal sense.

915. Extent of Self Medication. In 1905 it was estimated that between \$75,000,000 and \$100,000,000 were spent for patent medicines. In a report appearing recently it was stated that fully \$500,000,000 are spent annually for patent medicines in the United States.

The Purpose of This Part of the Chapter is not to condemn all patent medicines, but to try to show the student some of the underlying principles of the manufacture of patent medicines; the general nature of the habit forming drugs that are so often used; and to urge upon him the necessity of knowing something about what he is taking, if he prefers self medication to professional treatment.

916. Classification of Patent Medicines. While many patent medicines may be secured that claim to cure almost any disease, many make their strongest claim by pretending to cure certain specific diseases—several of which are *absolutely incurable by drugs* so far as is known to the medical profession at the present time, among which are cancer, consumption, epilepsy, and paralysis. A strictly ethical physician would not withhold any known cure for these or any other disease from other physicians, so that great care should be exercised in determining to trust to patent medicines aiming to cure such diseases.

917. Method of Discussion. The analyses referred to have been made either by the chemists of the American Medical Association, or by the Government chemists. The discussion will be more along the broader lines of the effects of certain kinds of drugs upon the system, and to point out the classes of patent medicines making use of these drugs. The student can decide for himself whether he wishes to purchase and use any particular patent medicine.

For obvious reasons no names of manufacturers or their medicines will be given in this chapter. The statements made may all be verified by referring to the various publications cited, some of which may be obtained free of charge from the Superintendent of Public Documents, Washington, D. C. and the others may be obtained from the American Medical Association, Chicago, Ill. The American Medical Association publishes annual reports on the analyses of various preparations under the heading "Annual Reports of the Chemical Laboratory of the American Medical Association." They will be referred to in this chapter as A. M. A. Vol. V, p. 1, etc. Another publication of the Association, reprinted from Collier's, is "The Great American Fraud." This will be referred to as G. A. F. Government publications will be cited by name and number.

918. Widely Advertized Concoctions Containing Alcohol. Beer contains 3.5 to 7.5% of alcohol by volume; wine from 9 to 17%; cider, from 3.5 to 7.5%; brandy, from the distillation of

wine, 44 to 55%; whisky, from the distillation of alcoholic liquids made from grains, 46 to 55%; rum, from 30 to 50%. The percentages by weight are approximately $\frac{4}{5}$ of these figures. Among various widely advertized medicines containing a large percentage of alcohol are some of the well known sarsaparillas, stomach bitters, blood bitters, catarrh cures, so-called vegetable compounds, wines, etc., the percentage of alcohol varying from 9 to 44. Needless to say the use of such compounds induces the liquor habit, and the government has wisely prohibited the sale of at least one of these to the Indians. (See circular of the Department of the Interior, dated Aug. 10, 1905.) This widely advertized, but prohibited medicine may be closely imitated by using alcohol, $\frac{1}{2}$ pint; water, $1\frac{1}{2}$ pints; with a little cubebs for flavor and some burnt sugar to give color. Since the Volstead act went into effect many of these "medicines" have been discontinued.

919. Medicines Containing Cocaine, Opium, Morphine, etc.

This class of medicines is particularly dangerous, since they are habit forming and the effects are even worse than those of alcohol. Since the Harrison Anti-narcotic law went into effect, March 1, 1915, the sale of this dangerous class of substances has been greatly lessened. A brief description of these drugs and their effects upon the system follows.

Cocaine. Cocaine at first produces stimulation, then depression of the different segments of the central nervous system, beginning with the brain and extending to the cord and the medulla. Respiration is at first quickened, then depressed until symptoms of respiratory paralysis appear. The heart is at first stimulated, later paralyzed. The blood pressure is at first raised, and the pulse accelerated, but later the blood pressure falls.

Opium is a concrete milky exudation obtained from the unripe capsules of the *papaver somniferum*, containing not less than 9% of morphine. It may be obtained as a very fine powder, when

the juice is dried at not more than 60° C. and ground. The powder contains 12 to 12.5% morphine.

Morphine is the alkaloid derived from opium. It has the formula $C_{17}H_{19}NO_3 \cdot H_2O$, and occurs as white prisms, having a silvery luster and bitter taste. The actions of morphine are three (1) a specific central analgetic action; (2) a depressant action on the entire central nervous system of a descending type; (3) a constipating effect. It is practically devoid of local action except on the gastro-intestinal tract. Central excitation may occur, followed by depression. Nausea and vomiting may occur, lasting for hours. It is usually used as the sulphate, $(C_{17}H_{19}NO_3)_2H_2SO_4 \cdot 5H_2O$. The respiratory center is depressed by relatively small doses of morphine, and use is made of this in cough syrups and so-called consumption cures, but if the cough is "productive" the depression of the cough reflex may cause a dangerous retention of secretions of the inflamed mucous membranes that should be expectorated.

Cocaine has been widely used in numerous so-called catarrh cures as well as in *soothing syrups for babies*. Other substances used in the latter class of medicines, in addition to cocaine, opium and morphine, were heroin, $C_{17}H_{17}(C_2H_3O)_2NO_3$; codeine, $C_{18}H_{21}NO_3 \cdot H_2O$, an alkaloid from opium; chloroform, $CHCl_3$; chloral hydrate, $CCl_3 \cdot CH(OH)_2$; and cannabis indica, commonly called Indian hemp. Farmers' Bulletin, No. 393, page 5, gives a list of 13 well known and widely advertized soothing syrups that contained one or more of these dangerous substances before the Harrison law became operative. See also Bulletin No. 401. Some of these have now been radically changed.

920. Cough and Cold Remedies, containing usually the same drugs as found in soothing syrups and sold indiscriminately, have been put on the market both as syrups and as lozenges and pastilles. See Farmers' Bulletin No. 393 for a list of these remedies. *Consumption cures* are in the same class, and have long offered an inviting field for quacks, since the victim of the

disease will usually buy anything to bring about a cure. Here especially the depression of the cough reflex is dangerous. The ravages of the disease are not checked and the secretions are absorbed instead of being expectorated, thus increasing the toxins in the body. A considerable list of consumption cures (?) may be made out if the student will consult Farmers' Bulletin No. 393, page 14; G. A. F. page 60; A. M. A. Vol. 3, page 102, 107; Vol. 4, page 67; Vol. 6, page 67. One analysis showed the mixture to consist of alcohol 44%, sulphuric acid 4%, and water 52%. Another was chiefly creosote and sugar; while a third was 16% alcohol, a dash of strychnine, and a little cochineal.

921. Headache Cures. Many headache remedies have been introduced since 1884. Antipyrine was first used that year, followed in 1886 by acetanilid and in 1887 by phenacetin, all of which affect principally the heart and circulation, and then other parts of the body. Blueness of the skin, particularly the lips and mouth, nose and ears, nails and finger tips, and other parts of the body if the dose is large, is common, due to destructive changes in the blood, leading to anemia, with the regular symptoms—pallor, shortness of breath, palpitation of the heart, muscular weakness, and disinclination to make any exertion. At first these remedies were used for reducing fevers, but owing to the weakening effects they were used more and more for the relief of pain—headache and other minor ills. These substances do not act as foods as often claimed, but acetanilid tends to impair the nutrition of the body. A report sent to 925 physicians, and answered by 400 showed 1669 cases of poisoning from the use of these drugs over a period of 24 years of which 55 resulted fatally, and with 169 cases of habitual use. In poisoning by acetanilid there is general weakness, dizziness, faintness, lividity of the face, a pinched and anxious expression, shortness of breath, great restlessness, sweating, coldness of the extremities, rapid and weak pulse, and in severe cases stupor and loss of consciousness. At one time it was thought that the depressing

effects of acetanilid were counteracted by caffein, but this was later shown to be erroneous.

Acetanilid, C_8H_9NO , or $C_6H_5NH(CO.CH_3)$, occurs as white, shining, crystalline scales, with a slightly burning taste. It is soluble in 180 parts of water at $25^\circ C$. and is also soluble in alcohol, ether and chloroform. When acetanilid is taken into the body it is changed into para-amino-phenol and this substance depresses the heart.

Antipyrine, $C_{11}H_{12}N_2O$, is a fine white crystalline powder, soluble in water, alcohol, chloroform and ether, and melting at 112.5° . A single dose of five grains or less may produce alarming symptoms in adults while a dose of 10 to 15 grains has produced serious consequences, some individuals reacting more easily than others. While antipyrine shows many of the same effects as caused by acetanilid poisoning, it also causes eruptions resembling hives, scarlatina, or measles, swelling of the face, temporary blindness, and abscesses.

Phenacetin, or *Acetphenetidín*, $C_{10}H_{13}NO_2$, is a white tasteless crystalline powder, soluble in 925 parts of water, and in chloroform and ether, in smaller amounts. It melts at 134° to 135° . Phenacetin was the result of chemical investigation to discover, if possible, some agent of the coal-tar class which would produce all of the desirable characteristics of acetanilid and be free from its undesirable effects. These results were only partially obtained for it produces many of the harmful effects and the general effects in cases of poisoning are about the same.

In *The Great American Fraud*, page 38, may be found a list of many well known headache cures, both "ethical" and "patent" that depend for their results upon the heart-depressing effects of acetanilid, and the article goes on to state that practically all of the drug store vended "headache cures" and "anti-pain" remedies depend upon this substance for their effects.

Codeine sulphate, $(C_{18}H_{21}NO_3)_2.H_2SO_4.5H_2O$, is used to replace opium and morphine to some extent and is found in a number of

headache mixtures. Farmers' Bulletin No. 393, page 15, mentions a number of headache cures as illustrations of this class, and states that the general effect is simply to benumb or stupefy the senses, but not to remove the cause of the trouble.

922. Epilepsy. There is no drug or mixture of drugs known to the medical profession which will eradicate epilepsy. The best they can do is to diminish the frequency of the attacks by certain medicines and by regulating the diet. However, a number of epilepsy cures are on the market, containing one or more bromides, but a number of them contain opium or morphine, the primary purpose of which is to create a demand for the remedy. Among these are the numerous so-called cures mentioned in *The Great American Fraud*. See also A. M. A. Vol. 8, pp. 52-79, where the subject of the analysis of epilepsy nostrums is discussed in detail, with special reference to their bromide and chloride content. Ammonium, sodium and potassium bromides seem to be the chief ingredients of these medicines, with sometimes small amounts of the bromides of calcium and strontium, or small amounts of the chlorides or carbonates. Alkaloids are not present to the same extent as in nostrums of the same kind before the passage of the Harrison narcotic act.

In the same way there is *no cure for cancer by the use of drugs*, yet there are several on the market, some of which are more fully discussed in G. A. F.

923. Obesity Cures must also be classed among the quack remedies. A. M. A., Vol. 5, page 60, describes one obesity cure as consisting essentially of sodium carbonate, magnesium sulphate, potassium nitrate and sodium sulphate, to be used as a bath powder. Another remedy for the same purpose (A. M. A. Vol. 5, page 89) was chiefly milk sugar and casein, and may be made from the evaporation of skimmed milk. A third remedy (A. M. A. Vol. 6, page 52) consisted of alcohol, 53.32%; soap, 3.61%; potassium iodide 12.01%; sugar, 12.87%; water and undetermined, by difference, 18.19%. The changes in the composition and the label of another obesity cure are fully described

in A. M. A. Vol. 6, page 57. A rather new remedy described in the same volume, page 63, consists of boric acid, 59.4%; corn starch, hydrous, 20.1%; milk sugar, hydrous, 12.6%; water, flavoring extracts, etc., by difference 7.9%. The statement is made that persons taking this remedy get about 9 grains of boric acid in each tablet, and that the use of these tablets will reduce obesity only in those instances in which the boric acid so seriously impairs the digestion that the patient loses weight from the resulting illness. Still another obesity cure is said to be duplicated by a mixture of powdered alum, 1 pound; alcohol, 10 ounces; water sufficient to make 1 quart. The analysis shows 0.16% sodium iodide. The cost of the duplication is not over 30 cents, but the remedy sells for \$20.00.

924. Hair Tonics aim to stimulate the growth of the hair, and thus appeal to the vanity rather than to vital processes, but some of them contain dangerous substances, such as paraphenylen-diamin, which should not be used since it tends to produce eczema. See A. M. A. Vol. 3, page 71; page 110; Vol. 6, page 55. Of these, one, advertized in such a manner as to make the reader believe that it contains quinine as its main ingredient, was found by analysis to contain only 0.02% quinine or cinchona alkaloids, just enough to escape prosecution under the federal Food and Drug Acts for misbranding.

925. Hay Fever. As an example of the difference in remedies for the same disease, one remedy for hay fever is said to contain 99.95% cocaine hydrochloride (See Notice of Judgment No. 323). Another remedy for the same disease, retailing for \$1.00 for about $2\frac{3}{4}$ ounces was found to be nothing but milk sugar, and no medicinal substances could be detected. See A. M. A. Vol. 4, page 79.

926. Sleeplessness. Hypnotic alkaloids, bromides, chloral, and other hypnotics such as diethyl-barbituric acid (veronal) and sulphon-methane (sulphonal) are often used to induce sleep. It would be natural to look for one or more of these

substances in any remedy professing to overcome sleeplessness, but in one remedy the essential ingredients turned out to be asafetida with gypsum and powdered capsicum, none of which have any value for the purpose mentioned by the advertisers. See A. M. A. Vol. 4, page 103.

927. One Eczema Lotion selling for \$2.00 a pint, was found by analysis to consist essentially of the following substances in each 100 cc. of the solution; mercuric chloride, 0.0463 gm.; mercuric nitrate, 0.0450 gm.; glycerine 1.3021 gm.; nitric acid, 1.0265 gm.; water, 98.5545 gm. The estimated cost of making it is 6 cents per gallon, or about \$2.00 per barrel. See A. M. A. Vol. 3, page 45.

928. Miscellaneous Preparations. One very widely known cure (?) for tired and "smelly" feet selling for about one cent per tablet is said to consist of alum, 60%; tannic acid, 10%; salicylic acid, 5%; talcum, 5%; starch, 20%. (A. M. A. Vol. 4, page 112.) These tablets were to be dissolved in warm water and the feet soaked thoroughly. Warm water alone will remove the tired feeling, and a little soap will remove the smell. Or a teaspoonful of formalin per pint of water may be used, drying without wiping. However, the ex-owner of the preparation is said to have cleared a million dollars from the sale of the tablets. and the final disposal of his interests.

One highly exploited new "elixir of life" is given several pages in A. M. A. Vol. 5, beginning on page 71. It is shown to be essentially casein, the chief part of cottage cheese, and the comment is made that one dollar's worth of wheat flour contains as much energy as \$197 worth of this wonderful preparation.

One "cure all" was formerly said to be effective in any disease where the cause was due to germs. One bottle was given free with the understanding that if benefited the user would purchase six more bottles. The regular selling price was fifty cents for a small bottle. A series of analyses carried out by chemists all over the United States showed that the remedy consisted essentially of water, nearly 99%; sulphuric acid, 0.9%;

sulphurous acid, 0.3%; with a little burnt sugar to color it. It cost about five cents per barrel to manufacture it.

The substances mentioned in the foregoing paragraphs are not all that might be studied with profit to the student. He probably agrees, however, that for satisfactory self medication he will need to exert great care not to become addicted to habit forming drugs, and he should watch carefully to see that he is not paying exorbitant prices for simple remedies. Probably self medication for minor ills is here to stay, so that if one does not care to visit a physician, but prefers to prescribe for himself, he should at least study the declared substances on the labels of the bottles, and then decide whether it is the thing required for his special ailment. If he cannot decide these points it is better to take the advice of a competent physician.

BRIEF BIBLIOGRAPHY

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Bush	Laboratory Manual of Pharmacology	F. A. Davis Co
Cow	Pharmacology	Churchill
Hallberg & Salisbury	Physicians' Manual of the Pharmacopeia and the National Formulary	American Medical Association
Hatcher & Wilbert	Pharmacology of Useful Drugs	American Medical Association
Lucas	Book of Prescriptions	Blakiston
Lucas & Stevens	The Book of Pharmacopeias	Blakiston
Ruddiman	Incompatibilities in Prescriptions	Wiley
Squibb	Materia Medica	E. R. Squibb & Sons
Street	Patent and Proprietary Medicines	American Medical Association
	Complete Medical Pocket Formulary	Lippincott
	Useful Drugs	American Medical Association

CHAPTER XXXIX

POISONS, TOBACCO, ALKALOIDS AND GLUCOSIDES

929. Poisons Defined. A poison may be defined as any substance that acts deleteriously upon the body, so as to produce sickness or death. It may be taken into the body through the mouth, through cuts or wounds, or by absorption through the skin or membranes, and the amount required to produce death may vary from a fraction of a grain to several ounces, depending upon the nature of the poison.

930. Poisons Classified. Poisons are generally classified (1) as to the source, whether inorganic or organic, and (2) as the effect upon the human system, whether corrosive, irritant, neurotic, etc. The following diagram thus classifies the common poisons:

- I. Inorganic
 - 1. Corrosive
 - a. Strong acids
 - b. Alkalies
 - c. Caustic Salts
 - 2. Irritant
 - a. Salts of potassium, sodium, barium, etc.
 - b. Metalloids—phosphorus, chlorine, bromine, iodine
 - c. Compounds of arsenic, antimony, mercury, lead, copper, tin, zinc, silver, iron, bismuth, chromium
 - 3. Vulnerants, as powdered glass, tacks, needles, etc., causing perforations in the stomach, bowels or heart.
- II. Organic
 - 1. Irritant
 - a. Animal
 - a) Snake and insect poisons

- b) Ptomaines, cantharides
- b. Vegetable
 - Aloes, colocynth, gamboge, jalap, castor oil seed, elaterium, croton oil, hellebores, savin, yew, ergot, hemlocks, laburnum arum, bryony, etc.
- 2. Neurotic
 - a. Somniferous
 - Opium and its alkaloids
 - b. Deliriant
 - Belladonna, hyoscyamus, stramonium, solanum, cannabis indica, cocaine, camphor, poisonous fungi
 - c. Inebriants
 - Alcohol, ether, chloroform, chloral, carbolic acid, nitro-benzol, aniline, benzene, turpentine, nitroglycerine
- 3. Sedatives or Depressants
 - a. Neural
 - Conium, lobelia, tobacco, physostigma, curara
 - b. Cerebral
 - Hydrocyanic acid, oil of bitter almonds
 - c. Cardiac
 - Aconite, digitalis, veratrum, colchicum
- 4. Excito-motory or Convulsives
 - Nux vomica, strychnine
- III. Asphyxiants
 - Poisonous and irrespirable gases

931. Effects of Different Classes of Poisons. *Effect of Corrosives.* Corrosives have a sour, acid, alkaline or metallic taste and produce a burning pain at once all the way from the mouth to the stomach. Vomiting occurs, either brown or black. Gases are emitted through the mouth, and there is cough, weak voice and great thirst. Collapse may occur, the pulse is small and rapid, and the victim is usually conscious until death.

Effect of Irritants. Irritants produce a burning pain, a feeling of constriction in the throat and pain in the stomach, with intense thirst. At first vomiting of food and bile occurs, but later altered blood is vomited. Purging occurs, with pain in the abdomen, hoarseness, cramps, collapse and fever.

Effect of Neurotics. Neurotics produce different effects, depending upon the nature of the drug taken. *Narcotics* produce giddiness, dimness of vision, headache, contraction of the pupils, confusion of thought, drowsiness, insensibility, coma and occasionally convulsions. *Delirians* produce active delirium, illusions of sight and hearing, dryness and redness. *Inebriants* produce great excitation of the brain, circulation and respiration, followed by staggering, double vision, mania, sleep, insensibility to pain, and death.

Effect of Depressants. *Neural depressants* cause paralysis of the spinal cord; *cerebral depressants* act by inhibiting the functions of the brain; *cardiac depressants* kill by sudden shock or collapse.

Excito-motory poisons cause twitchings and then convulsions.

932. A General Antidote is often administered where the nature of the poison is unknown, consisting of a mixture of different substances each intended for a certain purpose. As an example of general antidotes, 2 parts of powdered charcoal are mixed with 1 part each of tannic acid and heavy magnesium carbonate. The powdered charcoal absorbs alkaloids, tannic acid precipitates many metals and alkaloids, while magnesium carbonate neutralizes acids and hinders the absorption of arsenic. The dose is a large teaspoonful of the mixture.

Demulcents or Soothing Agents are administered for the purpose of overcoming the irritating effects of poisons, and consist of such substances as oils, starch, milk, the white of egg, etc.

Stimulants are administered where the heart is greatly depressed and consist of brandy, aromatic spirits of ammonia, etc.

Saline infusions are injected in cases of great collapse.

Purgatives such as castor oil cause bowel movements.

Pain is overcome by hypodermic injections of morphine.

Emetics produce an emptying of the stomach by vomiting. Ipecac, 30 grains; zinc sulphate, 30 grains; or copper sulphate, 10 grains; may be given in half a glass of warm water; or 1 tablespoonful of mustard in $\frac{1}{2}$ pint of warm water.

Sedatives are given where there is great excitation. These may consist of chloral, 30 grains; opium $\frac{1}{2}$ grain; potassium bromide, 2 drachms; or chloroform by inhalation.

933. Antidotes vary according to the nature of the poison. In general it may be said that acids are used as antidotes for alkalies, and alkalies as antidotes for acids, by neutralization. Some of the common antidotes are glacial acetic acid, liquor of ferric chloride, heavy magnesium carbonate, magnesium sulphate, 2 drachms, for lead or barium poisoning; amyl nitrite, 2 minims, for aconite and chloroform; nitroglycerine tablets, 1/100 grain; potassium permanganate, 2 grains; sodium bicarbonate, 10 grains; tannic acid, for alkaloids; hydrogen peroxide, for phosphorus; oil of eucalyptus for strychnine; apomorphine hydrochloride, 1/10 grain as an emetic; atropine sulphate 1/100 grain for aconite, morphine, pilocarpine, poisonous fungi, etc.; cocaine hydrochloride, 1/6 grain; digitalin 1/100 grain for aconite; morphine sulphate $\frac{1}{3}$ grain for belladonna; pilocarpine nitrate, $\frac{1}{3}$ grain for belladonna; strychnine sulphate 1/60 to 1/20 grain, for nicotine and tobacco.

934. Special Treatment for the different poisons may be given as follows:

Acetanilid. Emetic or stomach tube. Inject 1/25 grain of strychnine. Apply warmth to the body.

Acid, Carbolic. Stomach tube. Sodium sulphate, 1 ounce; magnesium sulphate, $\frac{1}{2}$ ounce; or saccharated lime water 1 ounce in three ounces of water. 1 drachm may cause death in from 3 minutes to 6 hours.

Acid, Chromic. Stomach tube with great care. Chalk $\frac{1}{2}$ ounce in $\frac{1}{2}$ pint of milk; followed later by olive oil, milk, gruel, or white of egg in water.

Acid, Hydrochloric. Plenty of water. Stomach tube with care. Sodium carbonate 2 drachms in 5 ounces of water; soap and water; calcined magnesia, $\frac{1}{2}$ ounce in $\frac{1}{2}$ pint of water or milk; chalk; dilute ammonia, or white of egg and water. 1 drachm may cause death within 24 hours.

Acid, Hydrocyanic. Cold water over the head and chest. Emetic. Brandy, artificial respiration; faradic current. Inhaling air saturated with the gas causes instant death. 30 drops of a very dilute solution cause death in 10 to 15 minutes. With more concentrated solutions death has occurred within 2 minutes. If a person poisoned with hydrocyanic acid lives for 30 minutes he may recover.

Acid, Nitric. Soap and water. Calcined magnesia, chalk, whiting, or sodium carbonate and water. Later, olive oil and white of egg. Morphine hypodermically. The fatal dose is from 2 to 4 drachms, death occurring within 24 hours.

Acid, Oxalic. Stomach tube with care. Chalk $\frac{1}{2}$ ounce in 5 ounces of water; saccharated lime water 4 drachms in 2 ounces of water, repeated every half hour until 8 doses have been given. Stimulants. Gruel. 1 drachm may cause death after many days. A large dose may be instantly fatal.

Acid, Sulphuric. Treat as for nitric acid. The fatal dose is from 1 drachm to 4 ounces depending upon the contents of the stomach, in 18 to 24 hours.

Aconite. Emetic or stomach tube. Subcutaneous injections of digitalis, 15 minims; later brandy, with warmth, friction and artificial respiration.

Alcohol. Stomach tube. Cold effusions applied to the head. Later hot strong coffee and warmth. Children have died from drinking 2 or 3 glasses of whisky. A half pint of methyl alcohol is sufficient to kill a man in from 1 to 2 days.

Alum. 2 to 8 drachms prove fatal.

Ammonium Hydroxide. Treat as for potassium hydroxide. 1 drachm has caused death in a few minutes, but usually several hours are required.

Aniline. Stimulants. Artificial respiration. Bleeding and intravenous injections of warm salt solutions, 1 drachm to the pint. Several drachms are usually required for fatal results, death occurring in a few hours.

Antimony. Stomach tube or emetics. Glycerine of tannic acid, 2 fluid dr. in 5 ounces of water; or tannic acid, 30 grains in 5 ounces of water, repeated if vomited. Strong tea or coffee. $\frac{1}{2}$ pint of milk, stimulants, heat and friction. 2 grains or less of tartar emetic have caused death, the usual time required being about 24 hours. Antimony chloride is not as dangerous, 2 ounces proving fatal.

Antipyrine. Stomach tube. Brandy. Subcutaneous injections of strychnine $\frac{1}{2}$ grain; warmth.

Arsenic. Emetic or stomach tube. Ferric hydrate. 2 grains may cause death in from 2 to 20 hours.

Atropine. Stomach tube or emetic. Brandy. 1 pint of strong hot coffee. Hypodermic injections of morphine, $\frac{1}{3}$ grain. Flicking, pinching, warm and cold douche. Heat, friction and artificial respiration.

Barium Salts. Stomach tube or emetic. Sodium sulphate 1 ounce, or magnesium sulphate $\frac{1}{2}$ ounce in 5 ounces of water; alum, 1 drachm in 5 ounces of water. Stimulants. Heat 1 drachm of barium chloride or barium carbonate has caused death within an hour.

Benzol. Stomach tube or emetic. Later brandy, and inhale ammonia. 3 drachms have caused death in about 18 hours.

Camphor. Stomach tube or emetic. Later ammonia, brandy, heat, or injection. 30 grains have caused the death of infants.

Cannabis Indica (Indian hemp). Stomach tube, emetic. Stimulants. Apomorphine hydrochloride.

Cantharides. Stomach tube. Emetic. Demulcents. Opium or morphine. 11 grains of the powder or 1 ounce of the tincture cause death in several days.

Carbon Dioxide. Fresh air, or oxygen. Artificial respiration. Ammonia vapor, stimulants and heat. Carbon dioxide proves fatal when it constitutes 10 to 15% of the air.

Carbon Monoxide. $\frac{1}{2}$ to 1% proves rapidly fatal. 2% is instantly fatal.

Charcoal Vapors. These consist of 20 to 25% carbon dioxide and 2 to 3% carbon monoxide, and act in the same manner as the separate gases.

Chloral Hydrate. Prevent sleep by wet towels. Emetic. Stomach tube. Heat on feet. Later hot strong coffee, artificial respiration. Oxygen. 20 to 30 grains prove fatal in from 6 to 10 hours.

Chlorine. Inhale ammonia, alcohol or hydrogen sulphide. Air or oxygen.

Chloroform, Inhaled. Unfasten clothing. Withdraw the tongue. Oxygen. Alcohol. Brandy. Enema. *Chloroform swallowed.* Stomach tube or emetic. Olive oil. Wet towels. Hot coffee. $\frac{1}{2}$ ounce may prove fatal, death not occurring until 30 hours or more have elapsed.

Coal Gas. Fresh air. Oxygen. Stimulants. Coffee. Ammonia.

Cocaine. Emetic. Stimulants. Amyl nitrite, inhaled. $\frac{2}{3}$ grain causes death.

Conium (hemlock). Emetic. Stimulants. Oxygen. Hypodermic injections of strychnine. 5 minims cause death.

Copper Salts. White of egg and warm water. Milk. Emetic. Stomach tube. Later, demulcents, morphine or laudanum and heat. 1 ounce of copper sulphate or $\frac{1}{2}$ ounce of verdigris will cause death in 4 hours up to several days.

Croton Oil. Stomach tube. Emetic. Stimulants. Tincture of opium. Heat, friction, hot fomentations on abdomen.

Digitalis. Emetic, tannin, 30 grains. Stimulants. Recumbent position. 30 grains of the leaves, 1 ounce of the tincture, or $\frac{1}{4}$ grain of digitalin prove fatal, the time required being usually several days.

Formalin. Small doses of highly diluted ammonia or ammonium acetate every hour.

Fungi. Emetic. Stimulants. Hypodermic injection of atropine sulphate 2 minims. The poison of toadstools is largely *phallin* and *muscarin*. Death occurs often in about 24 hours.

Hydrogen Sulphide may prove rapidly fatal if present in the air to extent of 1%. Treat as for carbon dioxide.

Iodine. Emetic. Stomach tube. Later, starch and water. Amyl nitrite. Morphine and hot fomentations. 20 grains of iodine or 1 ounce of the tincture will cause death, usually several days elapsing before death occurs.

Iodoform. Emetic. Stomach tube. Dilute solution of sodium bicarbonate. Stimulants. Hot pack. Subcutaneous injection of saline solution. 30 grains cause death in a few days, or death may be delayed for 2 or 3 weeks.

Lead Compounds. Stomach tube. Emetic. Magnesium sulphate, $\frac{1}{2}$ ounce, sodium sulphate, 1 ounce in 5 ounces of water. Dilute sulphuric acid, 30 minims in $\frac{1}{2}$ pint of water. Milk, white of egg and water; poultices on the abdomen, morphine, and later potassium iodide. 1 ounce or more constitutes a fatal dose.

Lime. Carbon dioxide, aerated water, acetic acid or vinegar, oil.

Mercuric Chloride (Corrosive sublimate). Stomach tube with great care. Flour and water or arrow root and water. White of egg, since the white of 1 egg will coagulate and combine with 4 grains of mercuric chloride; stimulants, hot blankets and bottles, later morphine. 3 grains have caused death. The usual time required is 3 or 4 days but it may occur within $\frac{1}{2}$ hour or be delayed for a week or more.

Nicotine. (Tobacco.) Stomach tube. Emetic. Stimulants. Warmth. Oxygen, strychnine, later stimulants. The nicotine contained in an old pipe has caused death. Death has occurred from sleeping among bales of tobacco, or from smoking a single pipeful. A few drops of nicotine will cause death in a few minutes.

Nitrobenzol. Stomach tube. Emetic. Oxygen. Subcutaneous injection of solution of atropine sulphate, 2 minims. From 8 to 10 drops have caused death in from 4 hours to 2 days.

Nitroglycerine. Recumbent position. Cold effusions. Later,

hypodermic injection of ergot, 3 minims, or atropine sulphate, 2 minims.

Nitrous Oxide, (Laughing gas). As for chloroform.

Opium. Apomorphine hydrochloride hypodermically. Stomach tube. Emetic. Wash the mouth with solution of potassium permanganate, diluted with 5 volumes of water, and leave 5 ounces in the stomach. Strong hot coffee 1 pint by the rectum. Ether, 60 minims, hypodermically. Ammonia or smelling salts. Oxygen. Constant walking. 4 grains of opium, or 1 drachm of laudanum will often cause death in 8 to 12 hours. On the other hand those who begin with very moderate doses are able to increase them gradually until excessive doses may be taken. Thomas DeQuincy took as his maximum 300 grains of opium or 9 ounces of laudanum.

Phosphorus. Stomach tube or emetic. Oil of turpentine 20 minims every half hour until 6 doses have been given; or hydrogen peroxide, 30 minims, repeated. Purgative. $\frac{1}{2}$ ounce magnesium sulphate. Avoid fats and oils. 1 grain of finely divided phosphorus has caused death in 4 hours. Death may, however, be delayed for several months.

Potassium Binoxalate. Treat as for oxalic acid. $\frac{1}{2}$ ounce may cause death within 8 minutes.

Potassium Chlorate. Stomach tube. Emetic. Demulcent drinks. Purgative warmth. 3 drachms may cause death in 5 hours, or the time required may be several days.

Potassium Cyanide. Stomach tube. Emetic. Ferrous sulphate, 5 grains in 5 ounces of water. Strychnine hypodermically. Ammonia vapor. Oxygen. Friction. Alternate hot and cold douches. $2\frac{1}{2}$ to 5 grains make a fatal dose.

Potassium Dichromate. Stomach tube. Emetic. Chalk, $\frac{1}{2}$ ounce in $\frac{1}{2}$ pint of milk. Heat. 2 drachms will cause death in 1 hour or more.

Potassium Hydroxide. Stomach tube with care. Vinegar or dilute acetic acid. Lemons. Olive oil. Potassium hydroxide and sodium hydroxide cause death by dehydrating and saponi-

Santonin. Stomach tube. Emetic. Stimulants. If in convulsions, potassium bromide and chloral. Later stimulants.

Savin. Emetic. Later demulcents, castor oil, opium or morphine.

Sewer Gas. Fresh air. Stimulants. Oxygen. Coffee. Heat.

Silver Salts. Sodium chloride $\frac{1}{2}$ ounce. Stimulants. White of egg with water. Milk. Thirty grains cause death in from 6 to 24 hours.

Sodium Hydroxide and *Sodium Carbonate* as potassium hydroxide. Forty grains of sodium carbonate will cause death within 24 hours.

Strychnine. Potassium permanganate wash for the stomach with 3 volumes of water every $\frac{1}{2}$ hour. Apomorphine hydrochloride, 5 minims. Potassium bromide, 1 drachm every half hour. Chloral hydrate, hypodermically. Later, inhale chloroform. Oxygen. Three grains of the extract, 30 grains of powdered nux vomica, or $\frac{1}{2}$ grain of strychnine cause death in from 10 minutes to 3 or 4 hours, occasionally to 6 hours.

Tartar Emetic (Potassium antimony tartrate). Stomach tube. Tannin, 30 grains. Vegetable astringents. Tea, coffee, and later stimulants.

Tobacco. Emetic. Tannin. Strychnine, $\frac{1}{20}$ grain. Stimulants. Recumbent position. See Nicotine.

Turpentine. Stomach tube. Emetic. Magnesium sulphate $\frac{1}{2}$ ounce. Demulcents. Later morphine.

Zinc Salts. White of egg. Sodium carbonate in dilute solution. Demulcents. Strong tea. Fomentations. Morphine. $\frac{1}{2}$ ounce of zinc sulphate causes death in 4 hours or more.

935. Tobacco is Composed of a large number of substances common to the vegetable kingdom, such as starch, cellulose, albuminoids, glucosides, resins, chlorophyll and many vegetable acids. Freshly cut leaves contain 80 to 90% of moisture. The normal percentage when ready for market is about 14% but often as high as 20% is found.

Nicotine, the characteristic constituent of tobacco, varies from 1 to 10%. Thick leaved varieties contain more than the thin; the top leaves more than the lower leaves; and the percentage increases with the growth. Dark colored varieties contain more nicotine than light, and the use of large quantities of nitrogenous manure increases the percentage. Nicotine has the formula $C_{10}H_{14}N_2$. It is a volatile liquid. As found in tobacco it occurs as the malate and citrate. It is pungent, colorless and hygroscopic and its poisonous nature causes large quantities of it to be used as insecticides. Nicotine and its salts may be precipitated from even dilute solutions by the use of alkaloidal reagents, such as gold chloride, iodine, picric acid, etc. Nicotine may be obtained from tobacco by extracting with water in some form of continuous extraction apparatus. Lime or soda solution is then added and the liquid is steam distilled, after which the nicotine is extracted with ether. Nicotine treated with a drop of formalin and then with a drop of nitric acid gives a rose red coloration.

The Organic Acids in Tobacco are chiefly malic, pectic, citric, and oxalic. Acetic, nitric and tannic acids are found to a smaller extent. These acids are combined with the nicotine and during the sweating process the nicotine is partly liberated from its salts and part of it escapes. Various other chemical changes occur at the same time.

The Cause of the Aroma is not definitely known, but is believed to be closely connected with the considerable reduction of the nicotine content of the leaf during fermentation. High nicotine content is often associated with poor aroma.

The Odor of the Smoke is due partly to the volatilization of aromatic compounds, and partly to chemical changes in the constituents. In tobacco smoke have been found nicotine, ammonia, pyridine, carbon monoxide, trimethylamine, butyric acid, and traces of nicotianin, hydrocyanic acid and formalin, in addition to carbon dioxide and water vapor.

The Ash varies from 10 to 25%, and is smallest in the light

tobaccos used for cigarettes, and greatest in the leaves used for cigars. Excluding sand, which may adhere to the leaf mechanically, the ash consists of potash, lime, magnesia, iron oxide, alumina, soda, carbonic, silicic, sulphuric and phosphoric acids, and chlorine. Potash, K_2O , may constitute 30% or even more of the ash. The magnesia and silica stand next while the other oxides occur in comparatively small amounts. The combined chlorine varies from a trace to 15%. From the large amount of potash found in the ash it may be seen that tobacco is an exhaustive crop.

Tobacco is Used in various forms, such as the cut, twist or roll, cake or plug, cigars, cigarettes and snuff. Snuff is sold as dry or moist; the dry being made from the stems and midrib and ground finer than the moist, which may contain a varying percentage of the leaves. The stalks are cut small and moistened with water or lime water. They are allowed to ferment for several months and are then ground, dried, flavored and sifted. The essential oils, ground orris root and ground Tonquin beans are used to flavor snuff.

936. Other Narcotics include a large number of substances known as *vegeto-alkaloids*. These are nitrogenous carbon compounds, possessing basic properties. They occur in plants usually as the salts of organic acids. The greater number of them contain carbon, hydrogen, oxygen and nitrogen, but in a few cases, as nicotine and coniine, oxygen is lacking. Alkaloids are distributed in different proportions throughout the plant. Very little is known about the actual mode of formation, but during the life of the plant the alkaloid is gradually deposited in the bark, while if the plant is cut down after flowering the alkaloid often accumulates in the root.

937. General Properties of Alkaloids. The alkaloids are usually solid and are mostly crystalline. A small number, including nicotine, coniine, and pilocarpine are liquid. Some are volatile and distil with water, although alone they boil at much higher temperatures, often without appreciable decom-

position. Alkaloids are mostly insoluble or slightly soluble in water. Alcohol is the best solvent. They are usually soluble in chloroform, but less soluble in ether, benzene, or amyl alcohol. Alkaloids combine directly with acids to form salts, usually crystalline, and often soluble in water or alcohol, but generally insoluble in ether or chloroform. Alkaloids nearly always act as monacid bases even when they contain two nitrogen atoms, but there are some exceptions, such as the cinchona alkaloids, of which quinine is a diacid base.

The following are the more generally known alkaloids—

Aconitine, $C_{34}H_{45}O_{11}N$, found in monkshood and wolfsbane, is a powerful poison, 1/20 to 1/50 grain having caused death.

Atropine, $C_{17}H_{23}O_3N$, is highly poisonous. It is used for dilating the pupils of the eyes. As little as one part in 130,000 will dilate the pupil of a cat's eye.

Hyoscyamine, $C_{17}H_{23}O_3N$, is an isomeride of atropine and acts in the same manner.

Scopolamine, $C_{17}H_{21}O_4N$, acts upon the eye more violently than atropine.

Berberine, $C_{20}H_{17}O_4N$, is not poisonous and is used as a tonic.

Coniine, $C_8H_{17}N$, found in hemlock has a very penetrating odor, and burning taste. It is a powerful poison.

Emetine, $C_{30}H_{44}O_4N_2$, is found in ipecacuanha (ipecac). In minute doses it acts as an emetic; in larger doses it causes collapse and death.

Gelsemine, $C_{20}H_{23}O_2N_2$, from the root of the wild jasmine, resembles coniine in action. It is highly toxic and acts upon the eye.

Hydrastine, $C_{21}H_{21}O_6N$, occurs in the root of *Hydrastis canadensis* to the extent of about 1.5%. It is used in medicine as an internal styptic.

Codeine, $C_{18}H_{21}O_3N$, resembles morphine, but is less poisonous.

Thebaine, $C_{19}H_{21}O_3N$, occurs in small quantities in opium.

Narcotine, $C_{22}H_{23}O_7N$, occurs to the extent of 5 or 6%, or

even more, in opium. It is not as strongly narcotic as morphine or codeine. It appears to exist in the plant in the free state.

Morphine, $C_{17}H_{19}O_3N \cdot H_2O$, is an alkaloid of opium, which is the evaporated sap of the capsules of the white poppy. Laudanum is an alcoholic extract of opium. Paregoric is dilute laudanum containing camphor. See §919.

Papaverine, $C_{20}H_{21}O_4N$, occurs with thebaine and narcotine.

Pilocarpine, $C_{11}H_{16}O_2N_2$, is a colorless oil, soluble in water, alcohol and chloroform.

Piperine, $C_{17}H_{19}O_3N$, is obtained from black pepper or white pepper. It is extracted with alcohol. The alcohol is distilled from the solution and the alkaloid is precipitated from the remaining aqueous residue, by adding an excess of potassium hydroxide to dissolve the greater part of the resin. The base is purified by crystallization from alcohol; or powdered pepper is mixed with milk of lime and boiled for fifteen minutes. It is evaporated to dryness on a water bath. Free piperine is extracted from the mass by boiling ether, and it is then crystallized from alcohol. Iodine in potassium iodide added to a solution of piperine in alcohol containing hydrochloric acid forms steel blue needles.

Quinine, $C_{20}H_{24}O_2N_2$, is obtained from cinchona bark. It is used chiefly as the sulphate or the hydrochloride. It is very bitter and is slightly fluorescent. Quinine may be detected by adding, gradually, weak bromine water or chlorine water to acidified quinine sulphate until a permanent faint yellow coloration is obtained. Ammonium hydroxide is added drop by drop until the color changes to green. If acidified the color changes to red. Quinine is somewhat irritant to the stomach and intestines and when absorbed causes ringing in the ears, but in moderate doses produces no other marked effects in healthy persons. It may be used as a tonic, but its chief use is in malaria.

Ricinine, $C_8H_9O_2N_2$, is the alkaloid found in castor oil seeds.

Sinapine, $C_{16}H_{25}O_6N$, is found in white mustard seeds.

Strychnine, $C_{21}H_{22}O_2N_2$, is found in *nux vomica*, *St. Ignatius beans*, etc. It is a violent poison, giving rise to tetanic spasms, owing to greatly increased excitability of the spinal cord. One-half grain is fatal.

Brucine, $C_{23}H_{26}O_4N_2$, occurs with strychnine but is more feeble in its action.

938. Glucosides. Substances known as glucosides exist almost exclusively in the vegetable substances. By hydrolysis involving the addition of water they are changed into sugar, chiefly glucose and rhamnose and another compound not belonging to the carbohydrate class. Some yield other carbon compounds, of which some are not yet identified. These changes are brought about by the addition of dilute acids but more easily by enzymes, which usually exist in the plant along with the glucoside. The majority of the glucosides are colorless, neutral crystals. One or two are basic and a few are acidic. They are usually soluble in water or alcohol but not in ether. It is thought that the purpose of the glucosides is to penetrate the plant cells and stimulate the protoplasm to greater activity.

Glucosides are prepared by destroying the enzyme, to prevent hydrolysis, and extracting the glucoside with water, alcohol, or ethyl acetate in a Soxhlet apparatus.

Among the more common glucosides are *digitalin*, $C_{35}H_{56}O_{14}$ or $C_{36}H_{58}O_{14}$, which acts upon the heart; *indican*, $C_{14}H_{17}O_6N \cdot 3H_2O$, found in woad and extracted by acetone; *saponins*, $C_nH_{2n-8}O_{10}$, closely analogous glucosides, having the property of dissolving in water and frothing strongly in emulsions with oil and resinous substances, preventing the deposition of finely divided substances; *sinabin*, $C_{30}H_{42}O_{15}N_2S_2 \cdot 5H_2O$, found in white mustard; *aesculin*, $C_{15}H_{16}O_9 \cdot 2H_2O$, which is found in the horse chestnut; *amygdalin*, $C_{20}H_{27}NO_{11} \cdot 3H_2O$, found in bitter almonds and in the seeds of apples, pears, peaches, plums, cherries, etc.; *tannins* which occur in oak bark, sumac, tea leaves, etc., and yield a green or blue color when treated with a

ferric chloride solution; *salicin*, $C_{13}H_{18}O_7$, which is found in willow bark and in the bark and leaves of poplars; and several others less well known.

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CHAPTER XL

CHEMISTRY IN WAR AND PEACE

939. The Methods of Fighting in Warfare began, like everything else, in a crude form, and have gradually evolved into a complex system hardly realized by the world at large. Clubs and stones gave way to the javelin and the sword, and the better swordsman always had the advantage in mortal combat. With the advent of black gunpowder the most skilful swordsman at a distance had no better chance of escaping death than the most ignorant camp follower; walls that could withstand the battering ram crumbled when assailed by modern cannon. Always, when new methods of fighting were introduced, the opposite side raised cries of unfairness, not realizing that the question of fairness does not belong to the method of fighting, but to the fundamental question of the justification of war except for defense. As long as new methods of warfare can be devised they will be used, and it is obvious to any one who has watched the progress of the World War, where the final outcome depended upon chemistry more than upon any other single factor, that in the next great war the nation or nations that have not profited from the lessons taught in the World War, and have not developed chemical methods of offensive and defensive fighting to the highest extent will have no chance to survive as a world power. Chemistry, probably aided by bacteriology, will produce invisible weapons of greater deadliness than any yet known. A nation, fighting for existence, and knowing these methods, knowing that it must survive or perish as a nation, will stop at nothing to win the war, and the nation unprepared or unwilling to fight with the same weapons must perish.

The object of this chapter is not to justify or glorify war, but by outlining briefly what has been done along chemical lines

in warfare, to show the student something of what may be expected if some method of stopping all wars is not discovered. Only a few of the many explosives used both in war and peace will be described. No attempt should be made by the student to duplicate any of the substances described. If he feels the desire to manufacture explosives and poison gases, he may find opportunity in one of the properly equipped government laboratories.

940. Explosives are solid, liquid or gaseous mixtures or chemical compounds which, when chemical action is set up by a blow, a flame or otherwise, generate suddenly large volumes of heated gas.

The rapidity of the explosion depends upon the chemical nature of the explosive, its physical condition, the conditions under which it is exploded, and the method of firing.

Practical explosives depend upon oxidation for the result, the oxygen being furnished by nitrates, chlorates, nitric acid or the NO_2 group. The substance oxidized is usually endothermic, the heat of decomposition contributing towards the expansion of the gaseous products of the explosion.

Among the factors influencing the explosion are (1) temperature, frozen nitroglycerine being less sensitive than the unfrozen; (2) confinement, which usually increases the effect, although mercury fulminate is not affected to any great extent by being confined. Explosions are brought about by a heated solid, a flame, friction, percussion, the electric spark or concussion from another explosion.

Explosives are used generally for disruptive or propellant effects. They differ widely in the intensity of the effect produced and also in the safety of handling.

941. Explosive Mixtures usually have the combustible and the oxidizing substance as separate ingredients, not in themselves explosive.

In the Nitrate Mixtures the oxygen is in rather close combination, and the mixture is not very sensitive, so that it requires a

strong disturbing agency to liberate it and the action is comparatively slow. The best known of the nitrate mixtures is

942. Ordinary Black Gunpowder, differing rather widely in the proportions of the ingredients used. In the United States, England, Russia, Sweden, Italy and Turkey, it is composed of 75% potassium nitrate, 10% sulphur and 15% charcoal. In China it is 61.5% potassium nitrate, 15.5% sulphur and 23% charcoal. Other countries using the same materials vary the proportions somewhat.

Manufacture of Black Powder. The raw materials are carefully purified, ground and mixed, and run through the incorporating mill, where the moistened mixture is rolled under heavy rollers, weighing about four tons, for 3 to 8 hours, making what is called "mill-cake." This is then broken into small pieces, then granulated and sifted for sizes, and glazed by revolving in large cylinders for several hours, either with or without the addition of one ounce of graphite per hundred pounds of powder. The powder is then carefully dried and again revolved to remove any dust produced in drying and finally blended so

as to secure a uniform product. 11,500,000 pounds were manufactured for the ordinance department during the war. For military purpose black powder containing about 74% potassium nitrate is used (1) for igniting the propellant charge of smokeless powder; (2) as a basic charge for expelling shrapnel shell; (3) in the manufacture of primers and fuses; (4) in saluting blank fire charges; (5) in time train rings and combination fuses and (6) in the mixtures with other kinds of powders for use in ammunition for small arms. Fig. 209 shows a loaded shot gun shell.



FIG. 209. A Loaded Shot Gun Shell.

Many Substitutes have been used for all or part of the charcoal; coke, coal, peat, sawdust, bark, bran, tan, sugar, starch, dextrin, gum, etc., having been tried in order to reduce the smoke, but these substances

usually reduce the inflammability, slacken combustion and leave a large residue. During the Spanish-American War in 1898 the American troops were provided with black gunpowder. The smoke and flame from every discharge serves as a very convenient marker for the enemy. Needless to say that if the United States had been fighting a power of first rank the result would probably have been vastly different. Smokeless powder is described in §954.

943. Other Nitrate Mixtures, to take the place of potassium nitrate are sometimes used. *Sodium nitrate* is cheaper and has a larger percentage of oxygen, but is too hygroscopic to use if the powder is to be kept for any time. This is due to the nitrates and chlorides of magnesium and calcium, which cannot be eliminated cheaply to permit its use on a commercial scale.

Barium Nitrate has a smaller percentage of oxygen, but has a higher specific gravity and therefore more oxygen, bulk for bulk, than potassium nitrate. It is the least hygroscopic, but is higher in price, and explosives containing it have a higher ignition point and are slower burning.

Ammonium Nitrate increases the initial velocity of the bullet. It has 60% of oxygen, but only $\frac{1}{2}$ of it is available for oxidation, so that the available oxygen is only about half that of potassium nitrate. The use of ammonium nitrate decreases the amount of solid residue and gives much less smoke than from ordinary gunpowder. A large number of explosives containing ammonium nitrate have been put on the market. The majority of them contain a large percentage of ammonium nitrate, from 85 to 90%, while several run as high as 95 or 96%. The remaining materials differ in the different mixtures.

Ammonal B, said to be one of the safest explosives known, is 94 to 96% ammonium nitrate, 2.5 to 3.5% aluminum, 2 to 3% wood charcoal, and 0 to 1% moisture. The products of the combustion are said to be harmless. The powdered aluminum protects the nitrate from moisture and shell may be stored for

ten years and remain in good condition. The oxidation of the aluminum sets free a large amount of heat.

944. Chlorate Mixtures contain a large percentage of oxygen but are extremely dangerous to manufacture or handle. They may be exploded by percussion, friction, or spontaneous combustion, if traces of acid are present. As an illustration of the last condition, a mixture of powdered potassium chlorate and sugar, powdered separately, will burn with explosive violence if a drop of sulphuric acid is allowed to fall upon it.

945. In Explosive Compounds, as distinguished from explosive mixtures, the combustibles, carbon and hydrogen, are in close contact with the oxygen, in the same molecule. The most important compounds contain nitrogen in loose combination with all or part of the oxygen so that the chemical equilibrium is unstable to a greater or less degree. When the exciting force is applied the molecule undergoes more or less complete internal combustion, with almost instantaneous evolution of highly heated gaseous products. Explosive compounds are, therefore, as a class, more sudden and violent in their action than explosive mixtures and cannot be deadened by varying the ratio of the combustible to the oxygen.

946. The Nitro Explosives are generally divided into the nitro-derivatives and the nitric esters, with various other classes, as the fulminates, amino, nitro-amino, and azo-derivatives.

Nitro derivatives, as a class, are more stable than nitric esters and are not liable to spontaneous decomposition if slightly impure, and are stable in relatively large quantities of acid. This is due largely to a more stable internal structure, with a lower percentage of oxygen, which leads to a less complete combustion. They are very difficult to explode by simple heating but may be exploded by the use of a detonator. Some of the higher derivatives, like nitrotoluene and nitrophenol, are among the most powerful high explosives known, but the lower members are used mostly in explosive mixtures, chiefly with ammonium nitrate, potassium chlorate and ammonium perchlorate.

947. Trinitrotoluene, T. N. T., was substituted for wet guncotton (§953) about 1908. Guncotton is apt to dry out and explode prematurely. It is made by the nitration of toluene and occurs as colorless or sulphur-yellow to buff needle-shaped crystals, becoming darker on exposure to light. It burns quietly with a smoky flame when ignited and cannot be exploded even by very strong percussion except locally, so that a rifle bullet may be shot through a mass of it without causing an explosion. Mercury fulminate is used as a detonator. Trinitrotoluene is less powerful than either picric acid or wet guncotton, but its effect at a distance is greater. Shells are usually filled with it by melting the compound and allowing it to solidify under pressure in the shell, thus increasing the density of the compound from 1.5 to 1.7. It is used in many ammonium nitrate safety explosives and may be used in connection with mercury fulminate as a detonator. T. N. T. is too powerful to be used in guns, but is especially adapted for torpedoes and bombs. Depth bombs, for destroying submarines, each containing 300 to 600 pounds of T. N. T., were used in large quantities during the war.

Another high explosive of the same class is trinitroaniline, T. N. A. This, however, is affected by moisture and emits fumes of NO_2 , making it less suitable for use.

Trinitroxylol, T. N. X., is a stable compound, and slightly inferior to T. N. T. A mixture of T. N. T., 40%, and T. N. X., 60%, is known as *Toxyl*. This is equal to T. N. T. under water. Amatol consists of T. N. T. 20%, and ammonium nitrate 80%. Explosive D is a mixture of ammonium picrate, black powder and T. N. T.

The first barrage in the North Sea consisted of mines filled with T. N. T., but later, when these were replaced, T. N. X. was used instead. Fig. 210 shows a floating mine and Fig. 211 shows an aerial bomb.

948. Trinitrophenol, called picric acid, may be used by itself as a high explosive, and to a limited extent in explosive mixtures. It is made by either direct or indirect nitration of phenol

(carbolic acid) and crystallizes as bright yellow plates or prisms. It is hard to explode by direct percussion but mercury fulminate causes it to explode readily. It does not contain enough oxygen for complete combustion, lacking 3.49% for forming carbon monoxide, and 45.41% for carbon dioxide, but when sufficiently detonated it is one of the most powerful explosives known, exceeding dynamite or compressed guncotton, especially when

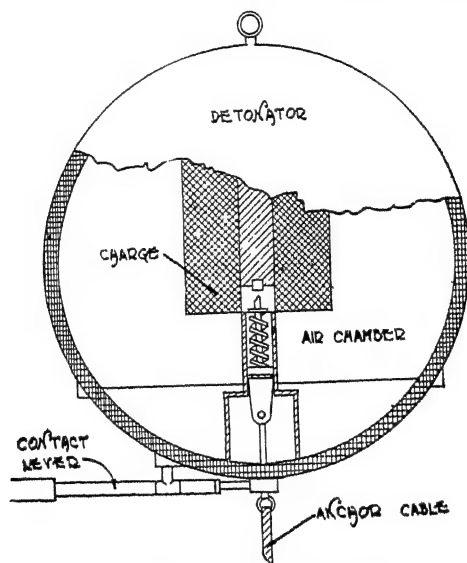


FIG. 210. A Floating Mine.

the density is increased by fusion and solidification under pressure. Picric acid was a favorite explosive of the French during the World War. The French Government imported large quantities from America. Picric acid is one of the peculiar explosives, in that it may be used very conveniently for other purposes. Thus a soldier might be fighting under a flag, part of which had been dyed yellow with picric acid; he might be struck with a shell filled with picric acid as the propellant agent; and

after being taken to the hospital might have his wounds disinfected and made less painful by the use of a picric acid solution. Picric acid solution is one of the very best remedies for burns. It deadens the nerve endings and soon relieves the pain.

Many explosives have been made with picric acid as the chief or only constituent, as *melinite*, *lyddite*, etc. Picric acid is safe to manufacture and transport, owing to its lack of oxygen, but when mixed with nitrates, chlorates, chromates or permanga-

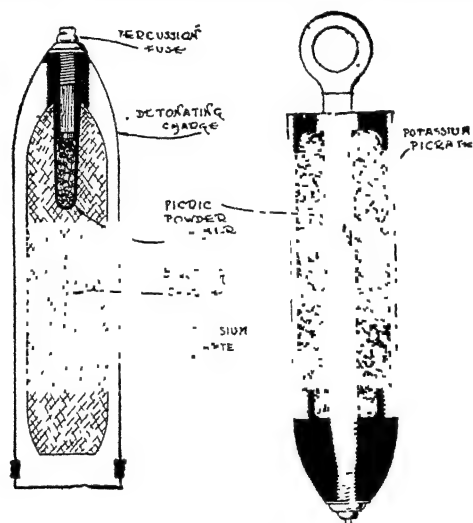


FIG. 211. An Aerial Bomb.

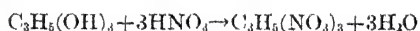
nates, extremely unstable mixtures are formed, liable to spontaneous combustion, owing to slow displacement of highly oxidized acids by the picric acid. The picrates of potassium, sodium and ammonium are usually quite stable under ordinary conditions, but are all more sensitive to heat, friction and percussion than the acid itself.

949. Nitric Esters are made by the nitration of organic alcohols and carbohydrates. The nitric esters are different from

the nitro compounds in internal structure and explosive violence, being less stable and more violently explosive, especially in the presence of foreign substances, such as traces of residual nitration acids.

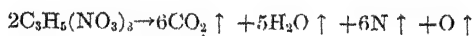
950. Of the Nitroglycerins the trinitric ester of glycerol is the most important. It is made by the nitration of glycerol in the presence of sulphuric acid, the glycerol being added to the mixed acids at such a rate as to keep the temperature below 22° to 25° . If red fumes are noticed the flow of glycerol is stopped and air is blown through until the fumes cease. If the red fumes cannot be stopped or if the temperature should rise above 30° and not fall with full air current on, serious local decomposition is indicated and the charge is at once drowned. Nitroglycerin is easily made, but is so exceedingly dangerous that it should never be attempted by the student.

The equation for forming nitroglycerine is



A theoretical yield of 247 parts of nitroglycerin per 100 parts of glycerol used should be obtained, but 230 parts give the limit actually obtained.

Nitroglycerin is a heavy oily liquid with a specific gravity of 1.60 at 15.6° . When pure it is colorless, but it is usually yellow to pale brown. It is neutral to indicators. When pure and free from water and acids it may be kept for years, but decomposition starts if traces of water or acid are present, if it is exposed to sunlight, or if the temperature rises as high as 45° to 50° . The temperature for explosion is stated to be from 180° to 200° . The equation showing the detonation for nitroglycerin is given as



951. Dynamites are divided into three classes, (1) where the absorbent material, or base, is inert; (2) where it is combustible; (3) where it is explosive.

Of the first class kiesel-guhr or *infusorial earth dynamite* is the best known representative and is always meant when dynamite is mentioned, unless some other kind is designated. Kiesel-guhr is from 95 to 98% silica, SiO_2 . From 20 to 30% of kiesel-guhr is mixed with 70 to 80% of nitroglycerin. The mixture forms a plastic pasty substance, from pink or gray to dark brown in color. Its specific gravity is about 1.6. Dynamite burns quietly with a yellow flame, but if much is ignited the temperature of the rest is apt to rise above the temperature of explosion, 180° , and detonation follows. Dynamite freezes at 4° , and like nitroglycerine is less sensitive when frozen. In order to neutralize any possible acid, from 0.5 to 1.0% of anhydrous sodium carbonate is often added to the dynamite. Fig. 212 shows the

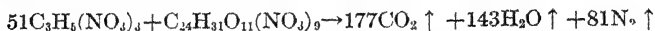


FIG. 212 Blasting a Stump with Dynamite.

use of dynamite for blasting. The Frontispiece shows the explosion of 600,000 pounds of dynamite in Baltimore Harbor.

Dynamites Containing Nitric Esters. Warm nitroglycerin will dissolve 7 to 8% of collodion cotton to form a plastic jelly, impervious to water. This is known as blasting gelatin. The nitroglycerin has an excess of oxygen and this is used to com-

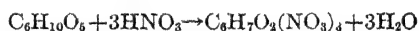
plete the combustion of the nitrocotton which is deficient in oxygen. The equation for the complete combustion is



It is suitable for military purposes but is too violent for mining although the violence may be reduced by kneading it with an absorbing powder, such as wood pulp, rye flour, and either potassium nitrate, sodium nitrate or ammonium nitrate, the last named making the explosive more powerful. Many modifications are made.

952. Nitrocelluloses. *Guncotton* is made by immersing cleaned cotton in mixed sulphuric and nitric acids, and after enough has been absorbed it is allowed to stand 24 to 48 hours to complete the nitration, and the guncotton is washed to remove the excess of acid. The washing may be accomplished in two or three days if the cotton has been reduced to a pulp, otherwise it takes six or more weeks.

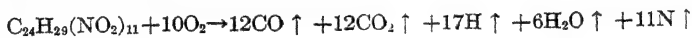
Cellulose has the formula $\text{C}_6\text{H}_{10}\text{O}_5$, and when it is converted into guncotton the equation is



953. Dinitrocellulose $\text{C}_6\text{H}_8\text{O}_3(\text{NO}_3)_2$, is less highly nitrated and is soluble in a mixture of alcohol and ether, and is known as collodion cotton. Usually finer qualities of cotton waste are used with weaker acids at a higher temperature of nitration. For collodion cotton the acid mixture is usually 66% sulphuric acid, 23% nitric acid, and 11% water, and nitration is carried on for an hour to an hour and a half at a temperature of 40° . Formerly very concentrated acids were used for guncotton but later investigations show that a mixture containing up to 12% of water may be used and that the addition of the water increases the stability of the product. Guncotton is insoluble in hot or cold water, alcohol, ether or glacial acetic acid, and unlike collodion cotton it is also insoluble in a mixture of alcohol and ether. It is soluble in acetone, ethyl acetate, nitrobenzene, etc.

Dried Guncotton burns with a long fierce flame without smoke. When in the form of yarn it explodes at 150° if heated rapidly. It is also exploded by percussion, but the explosion is only local when struck with an iron hammer upon an iron anvil. Wooden boxes containing guncotton may be perforated by a rifle bullet without exploding, although they are usually inflamed, but dynamite and other nitroglycerin preparations are exploded under the same conditions.

The Products of Complete Combustion, when fired in a closed vessel, vary somewhat in their relative proportions, depending upon the density of the charge, i.e. the ratio of the volume of the guncotton to the volume of vessel, and as the density of the charge increases, the proportion of carbon monoxide and water decreases, while that of carbon dioxide and hydrogen increases, tending to approach the following when Berthelot's formula for guncotton is used:



Guncotton may be detonated when either dry, wet or frozen, by mercury fulminate, but if it is wet it requires a much larger amount of the fulminate unless a priming of dry gun cotton is used. The use of guncotton is limited almost exclusively to military purposes, as in offensive torpedoes, submarine mines, etc. It is also used in certain mixtures, the most interesting of which are

954. Smokeless Powders, of which there are many varieties. The general principle in the manufacture of smokeless powders is to gelatinize the nitrocellulose thoroughly so that its fibrous character is destroyed. The powders are more or less hard, homogeneous colloids, which burn progressively from the surface so that their combustion is under control.

Smokeless and Semi-smokeless Powders are divided roughly into (1) nitrocellulose powders, from collodion cotton, gun cotton or both; (2) nitrocellulose powders with oxidizing salts, such as a powder of class (1) mixed with a metallic nitrate;

(3) nitrocellulose nitroglycerin powders, by combining a powder of class (1) with nitroglycerin; (4) nitrocellulose powders with another nitro derivative, with or without nitroglycerin and metallic nitrates. The first and fourth classes are used for military purposes, the fourth being more powerful than the first, since the nitroglycerin supplies the oxygen lacking in the nitrocellulose, therefore, a smaller charge and a smaller gun may be used for the same results.

Other Ingredients are sometimes added (1) deadeners, as camphor, vegetable oils, paraffin, vaseline, etc., to reduce or to control the rate of combustion of the explosion; (2) stabilizers to combine with any acid developed on storage. Diphenylamine and aniline act as stabilizers and also as indicators to show local spots or patches of peculiar colors caused by partial decomposition; (3) cooling agents, such as alkaline bicarbonates, carnauba wax, beeswax, guanidine nitrate, etc., which are added to form incombustible gases, to mix with the combustible gases and to protect them from the atmosphere until their temperature has fallen below the ignition point. However, adequate cooling agents really suitable for decreasing the flame almost invariably decrease the ballistic power and nothing is known that is entirely suitable for guns of large caliber.

The Solvents for the nitrocottons are generally acetone, ethyl acetate or amyl acetate for gun cotton, and a mixture of alcohol and ether for collodion cotton. Too rapid evaporation causes curling and blistering. Too much solvent makes the powder hard to dry, and too little causes imperfect solution and mixing. The deadeners, stabilizers and cooling agents are generally dissolved in the solvent before it is added to the nitrocotton. Only very small quantities remain in the powder after it is finished.

Smokeless powders are very insensitive to shock and percussion, and are not fired by the passage of a bullet through them. Even a strong detonator does not explode them unless

much unabsorbed nitroglycerin is present. Smokeless powders are somewhat difficult to ignite and sometimes ignite irregularly.

955. Fulminates of many of the heavy metals have been made, but only mercury fulminate is in practical use, the others being too sensitive and unstable.

Mercury fulminate is made by mixing alcohol and mercury in an excess of nitric acid. One method uses 3 parts of mercury by weight added to 30 parts of nitric acid having a specific gravity of 1.34. This is poured into a large flask containing 19 parts of alcohol. After some minutes violent action begins. Towards the end of the reaction 2.38 parts and later 1.58 parts of alcohol are added. The fulminate is thoroughly washed and dried. Mercury fulminate is usually light brownish gray in color, but is sometimes white. It is usually stored in linen bags, immersed in water from which it is taken out and dried at a temperature of not higher than 40° when it is needed. Dry mercury fulminate explodes violently when struck a moderate blow or by friction. When confined even between sheets of paper mercury fulminate explodes violently when ignited. It can be exploded by heating to 150° or over, by the electric spark or by sulphuric acid, and the equation for its decomposition is given as



The pressure produced by the explosion is about twice that produced by the explosion of nitroglycerin and about three times that of guncotton.

Mercury fulminate is used in percussion caps, mixed with potassium chlorate, powdered glass, antimony sulphide, etc. 0.22 to 0.25 grain of the mixture per cap being used for black gunpowder, and 0.6 grain for the smokeless powders.

956. Only a Few of the Many Gases Used, or possible to use in warfare will be described. To be successfully used as an offensive gas in warfare a gas must possess several important properties:

- (1) It must be highly toxic.
- (2) It must be readily manufactured in large quantities.
- (3) It must be readily compressed to a liquid, and must readily volatilize when the pressure is removed.
- (4) Its specific gravity must be greater than that of air.
- (5) It must be stable in the presence of moisture and various chemicals.

Chlorine and its use in warfare has been described in §§218 ff. It was found, however, that protection against chlorine was very easy to secure and from that time more deadly gases were used by both sides.

957. Phosgene is a mixture of chlorine and carbon monoxide. The mixed gases are passed over a carbon catalyst, combining with much heat. The phosgene is condensed to a liquid by passing it through pipes immersed in cold brine. When the pressure is removed the liquid vaporizes. It is a gas of high toxic power. Even after the effects have apparently disappeared it may produce severe delayed action upon the heart, resulting in death. Protection against phosgene is afforded by sodium phenate or sodium sulphanilate. Glycerin is usually added to prevent action upon the flannel of the gas masks.

958. Among the Lachrymators is Chloropicrin. This is made by the action of bleaching powder upon calcium picrate in wrought iron digesters, provided with condensers. It is a strong lethal gas and is used alone or mixed with stannic chloride or with phosgene. Chloropicrin, and some of the other lachrymators, cause slight irritation of the nose and throat when first encountered, and these effects often pass off after a short time; but in 4 to 8 hours the victim is attacked by violent coughing and the respiratory organs are so severely affected that the victim is helpless. Unless medical aid is immediate, death is almost certain to result from choking. Chloropicrin was also known as vomiting gas.

959. Tear gases include such substances as *xylyl bromide*, which has an effect like onions only much worse. When the

concentration of the gas is as little as 1 part in 1,000,000, such copious weeping is caused by the gas that the eyes cannot be kept open. This was called by the Germans *T shell* or *T stoff*. As used by the Germans it was not pure but contained much benzyl bromide, made by the action of a bromide upon coal tar light oil, from which most of the toluene had been removed for *T. N. T.*

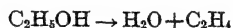
Other lachrymators include bromethylmethylketone, and the *K shell* gas, monochloromethylchloroformate. These are much more poisonous but do not hang around as much as xylol bromide after they are released.

Green X shell contained trichloromethylchloroformate. This is as poisonous as phosgene and is also known as *diphosgene*. It has very little effect upon the eyes. It has a smell resembling the earth or damp hay when dilute, but when the gas is concentrated it quickly asphyxiates, and is very deadly.

960. Sneezing Gas, or diphenylchloroarsine, is a solid substance that is atomized into tiny particles. It was often embedded in *T. N. T.* and shell thus filled were called *Blue X shell*. Violent sneezing is produced, so that the gas mask must be removed.

961. Mustard Gas, or dichlorethyl sulphide, is a water white liquid, boiling at 219°. It was first prepared by the German chemist, Victor Meyer, in 1886. Mustard gas was first used at Ypres, July 20, 1917. The Allies at once began to investigate methods of manufacture. It was not until February, 1918 that word came from England that it could be made by the absorption of ethylene gas in sulphur monochloride.

When alcohol is heated to a high temperature in the presence of a catalyst, such as kaolin, the alcohol is dehydrated to give ethylene.



Alcohol vapor and steam in equal volumes are introduced into an 8-inch iron pipe with a 3-inch core in contact with clay

at a temperature of 500° up to 600°. Later methods used phosphoric coke, (coke drenched with phosphoric acid), instead of clay, but this was not widely adopted, because the first method was satisfactory, although it was claimed for the newer method that it would give 2,000 cubic feet an hour of 98 to 99% pure ethylene.

The ethylene gas is dried, and then at a temperature of 60° is passed into sulphur monochloride, S_2Cl_2 , until further absorption ceases. Rapid agitation is necessary. When saturation is complete, it is treated with ammonia, causing the excess sulphur to precipitate, and the clear liquid remaining is sent to the shell-filling plants.

In addition to the serious effects produced by breathing the fumes of mustard gas, the liquid penetrates the clothing, the best protection being the use of oiled clothing.

962. Liquid Fire consists of a stream of burning oil forced out of a tank by compressed nitrogen. Its maximum effective distance was not more than 30 yards. It produced great quantities of flame and smoke, intense heat and was noisy, but did not do much damage, because the heat caused the flames to rise, and even a very low shelter afforded protection.

963. Gas Masks were needed by both sides, for if there should be a sudden shift of the wind, the gas might be blown back upon the side trying to use it. The gases used were sometimes released from cylinders, either with or without the use of siphons, or shot toward the enemy in shell. If the Germans had been equipped with the proper gas masks when they launched their first gas attack, they probably would have accomplished what they intended, for it is said that 90% of the allied army in the sector attacked was rendered unfit for service. But the Germans did not finish their preparations sufficiently, and had to wait until the gas had blown away before they could follow up the great advantage they had gained, and by the time they were ready to make their attack, the allied soldiers had recovered sufficiently to be able to repulse the attack. After that time

the call went out for protective gas masks, and they came by the million. As explained in the sections on chlorine, 218 ff. the first absorbent consisted of sodium thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3$, which will react with chlorine to give common salt, NaCl . After other gases were used, however, other materials were used in the more elaborate gas masks that were required. After experiments were tried on a large scale it was found that activated charcoal either with or without soda lime offered the best protection. See Figs. 213 and 214.



FIG. 213. An Army Gas Mask.

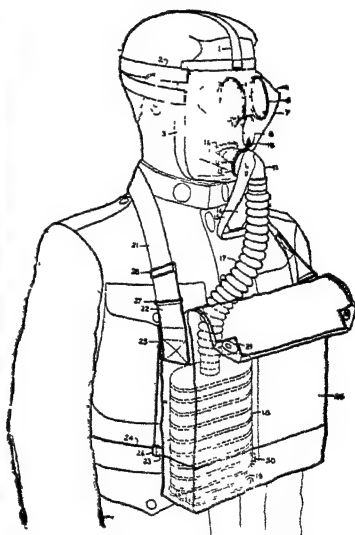


FIG. 214. Diagrammatic Section of Gas Mask

The activity of the charcoal apparently increased with the density of the raw material used. Coconut hulls had the highest density, and were used very extensively, but since they could not always be obtained with sufficient promptness, the stones of peaches, plums, etc., were also used. The coconut hulls were distilled at a temperature of 850° to 900° . They were then air

treated by repeated absorptions and evacuations, and ground so as to pass through an 8 to 14 mesh sieve. The ground particles were then activated with steam in nichrome tubes, and became about twice as active as the untreated charcoal. The charcoal from mixed nuts, while good, was not as satisfactory.

For most gases the charcoal was used in connection with soda lime. Charcoal alone was found to be satisfactory for gasoline, benzol, carbon disulphide, carbon tetrachloride and cyanogen chloride. Soda lime alone could be used against sulphur dioxide hydrocyanic acid, hydrogen sulphide, hydrochloric acid, and other acid gases. When toxic smokes were used the gas masks also contained two pads of cotton wadding. The life of the absorbing material naturally depended both upon the gas used and the concentration, sometimes requiring refilling at 10 minute intervals, and again lasting for several hours.

964. Among the many other ways in which chemistry contributed to the winning of the war were the use of smoke producers, marker shell, pyrotechnic signals, star shell, smoke shell, incendiary bombs and the development of the helium industry to furnish a gas to replace hydrogen for filling balloons.

White smoke for concealing military operations may be produced by the burning of yellow phosphorus, but it is dangerous to handle and gives offensive fumes. A later method of producing white smoke was in the use of anhydrous ammonia and silicon tetrachloride. These substances were contained in drums, charged with carbon dioxide under pressure to force out the liquids. When the fumes of the two mixed a white smoke, very persistent, but harmless, resulted.

Anti-dimming composition to use on the inside of gas masks offered another field for chemical research. Flashless powder to use at night is still wanted, and there are countless other places where in the next great war the chemist will make himself felt even more than in the past.

965. Now that the war is over, some of the excess products are being used in the arts of peace. Cordite is being manu-

factured into artificial leather, §885. Poison gases freed over a large area by the use of an airplane or automobile are used to destroy insect pests on fruit trees. High explosives intended for war uses are employed in removing obstructions, excavating, etc. While the chemists have turned their attention to more peaceful pursuits, many plants and laboratories working on a peacetime footing can be turned into war agencies at short notice, and a better knowledge of what can be accomplished by chemistry in times of war is possessed by all branches of the Government. See Figs. 215, 216 and 217. Let us hope that the lessons learned during the World War will not be forgotten, and that the development of chemistry as the handmaid of peace may not be interrupted again by the calls of war; but if the need comes new and still more destructive chemical weapons will be developed until war is made so horrible that no nation that wishes to exist will dare to start a war.

Note. The bibliography for this chapter is on page 666, top.

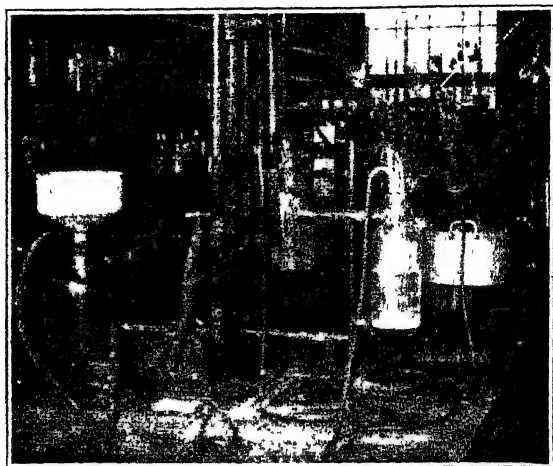


FIG. 215. Part of the Testing Laboratory of the Eastman Kodak Co.

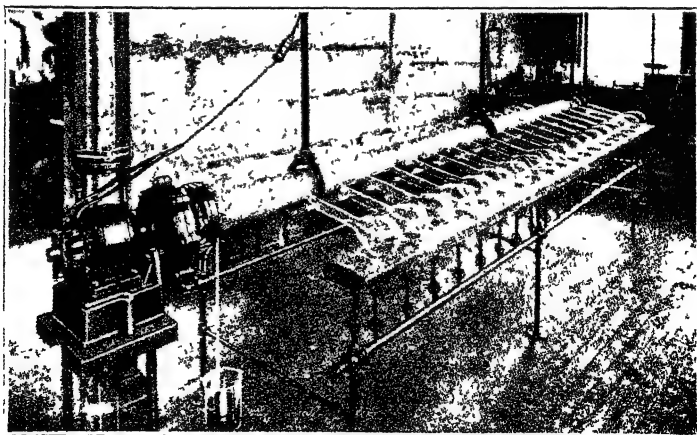


FIG. 216. Testing Laboratory of the Buckeye Cotton Oil Co.

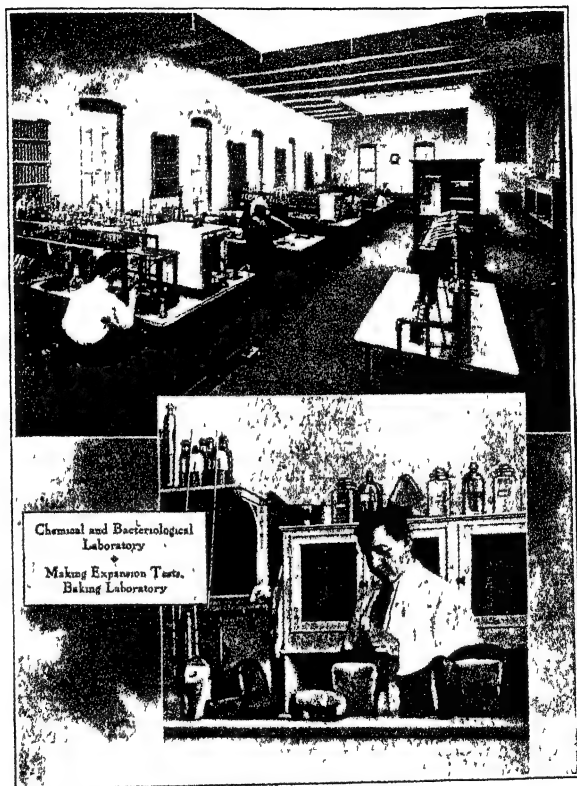


FIG. 217. Chemical, Biological and Baking Laboratory of the Fleischmann Co

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Davis	Handbook of Chemical Engineering	Davis Bros.
Gernsbach	1001 Formulas	Experimenter Pub. Co.
Hiscox	Recipes, Formulas and Processes	Henley
Martin	Industrial Chemistry, Inorganic	Appleton
Martin	Industrial and Manufacturing Chemistry	Crosby- Lockwood & Son
Meade	Chemists' Pocket Manual	Chemical Pub. Co.
Molnari	General and Industrial Chemistry	Philadelphia Book Co.
Molnari	Chemistry	Churchill
Morley & Muir	Watt's Dictionary of Chemistry	Longmans
Olsen	Van Nostrand's Chemical Annual	Van Nostrand
Rogers-Aubert	Industrial Chemistry	Van Nostrand
Stillman	Engineering Chemistry	Chemical Pub. Co.
Thorpe	Dictionary of Applied Chemistry	Longmans
Thorpe	Outlines of Industrial Chemistry	Macmillan
Villavecchia	Treatise on Applied Analytical Chemistry	Blakiston
	The Condensed Chemical Dictionary	Chemical Catalog Co.
	Scientific American Encyclopedia of Formulas	Scientific American Pub. Co.

There are so many excellent reference works in chemistry at the present time that merely to give a list of them would require too much space. The publishers of the works named in the bibliographies at the ends of the chapters will be glad to send catalogs listing many other books on these and other chemical subjects.

APPENDIX

TABLES OF SPECIAL VALUE IN THE STUDY OF CHEMISTRY

TABLE 1. AQUEOUS VAPOR TENSION

<i>Temp.</i> <i>C°</i>	<i>Tension in</i> <i>mm. of</i> <i>Mercury</i>	<i>Temp.</i> <i>C°</i>	<i>Tension in</i> <i>mm. of</i> <i>Mercury</i>	<i>Temp.</i> <i>C°</i>	<i>Tension in</i> <i>mm. of</i> <i>Mercury</i>
-10	2 09	12	10 46	26	24.99
- 5	3 11	13	11 16	27	26 51
0	4 60	14	11 91	28	28.10
1	4 94	15	12 70	29	29.78
2	5 30	16	13.54	30	31 55
3	5 69	17	14 42	35	41 83
4	6.10	18	15 36	40	54 91
5	6 53	19	16 35	50	91.98
6	7 00	20	17 39	60	148.79
7	7.49	21	18 50	70	233.09
8	8.02	22	19 66	80	354.64
9	8 57	23	20 89	90	525.45
10	9 17	24	22 18	100	760.00
11	9.79	25	23 55		

TABLE 2. TENSION OF MERCURY VAPOR

<i>Temp.</i> <i>C°</i>	<i>Tension in</i> <i>mm. of</i> <i>Mercury</i>	<i>Temp.</i> <i>C°</i>	<i>Tension in</i> <i>mm. of</i> <i>Mercury</i>	<i>Temp.</i> <i>C°</i>	<i>Tension in</i> <i>mm. of</i> <i>Mercury</i>
100	0.75	180	11 00	260	96 73
110	1.07	190	14 84	270	123 01
120	1 53	200	19 90	280	155 17
130	2 18	210	26 35	290	194 46
140	3.06	220	34 76	300	242 15
150	4 27	230	45 35	310	299.69
160	5.90	240	58.82	320	368 73
170	8 09	250	75 75	330	450 91

TABLE 3. BAROMETER CORRECTIONS

To be subtracted if the temperature is above 0°

<i>Temperature Degrees</i>	<i>Correction for Barometer with Glass Scale</i>	<i>Correction for Barometer with Brass Scale</i>	<i>Temperature Degrees</i>	<i>Correction for Barometer with Glass Scale</i>	<i>Correction for Barometer with Brass Scale</i>
5	0 7	0 6	25	3 3	3 1
10	1 3	1 2	30	4 0	3 7
15	2 0	1 9	35	4 7	4 3
20	2 6	2 5			

TABLE 4. CORRECTIONS FOR LATITUDE

To be added if the latitude is less than 45, and subtracted if the latitude is more than 45

<i>Latitude</i>	<i>Correction</i>	<i>Latitude</i>	<i>Latitude</i>	<i>Correction</i>	<i>Latitude</i>
0	1 97	90	25	1 27	65
5	1 94	85	30	0 98	60
10	1 85	80	35	0 67	55
15	1 70	75	40	0 34	50
20	1 51	70	45	0 00	45

TABLE 5. CORRECTIONS FOR ALTITUDE

To be added

<i>Altitude in Meters</i>	<i>Correction</i>	<i>Barometer Reading</i>	<i>Altitude in Meters</i>	<i>Correction</i>	<i>Barometer Reading</i>
300	0 04	720	1200	0 16	660
600	0 08	700	1500	0 19	640
900	0 12	680	2000	0 24	630

TABLE 6. SOLUBILITIES OF SALTS

	Acetate	Arsenate	Ironnile	Borate	Dymide	Carbonate	Chlorate	Chloride	Chromate	Cyanide	Ferricyanide	Ferrocyanide	Fluoride	Hydroxide	Iodide	Nitrate	Oxalate	Oxide	Phosphate	Sulfate	Sulfide	Tartrate
Ag ⁺	W	(A)	(A)	W(A)	N	(A)	Wh	N	(A)	(A)	I	I	W	(A)	N	W	(A)	(A)	(A)	W	(A)	(A)
Pb ²⁺	W	(A)	(A)	(A)	A	A	Wh	Wh	A	(A)	I	I	Wh	(A)	Wh	W	(A)	(A)	(A)	I	(A)	(A)
Hg ²⁺	W	(A)	(A)	(A)	A	A	A	A	(A)	W	I	I	Wh	(A)	A	W	(A)	(A)	(A)	W	AR	A
Hg ²⁺	W	(A)	(A)	(A)	A	A	W	W	A	A	I	I	Aso	(A)	A	WA	A	A	A	AW	AR	A
Cu ²⁺	W	(A)	(A)	(A)	W(A)	A	W	A	A	A	W	W	Aso	(A)	A	WA	A	A	A	WA	(A)	W
Bi	W	(A)	(A)	(A)	W	A	W	A	A	A	W	W	Aso	(A)	A	W	A	A	A	W	(A)	A
Cd	W	(A)	(A)	Aso	W	W	W	W	A	W	A	A	Wh	(A)	A	W	A	A	A	W	(A)	A
Au	W	(A)	(A)	W	W	W	W	W	A	W	A	A	(A)	(A)	I	W	W	A	W	(A)	(A)	A
Pt	W	(A)	(A)	W	W	W	W	W	A	W	A	A	(A)	(A)	I	W	W	A	W	(A)	(A)	A
As ³⁺	W	(A)	(A)	W	W	W	W	W	A	W	A	A	(A)	(A)	I	W	W	A	W	(A)	(A)	A
Sb	W	(A)	(A)	W	W	W	W	W	A	W	A	A	(A)	(A)	I	W	A	A	A	W	(A)	A
Sn ²⁺	W	(A)	(A)	W	W	W	W	W	A	W	I	N	W	(A)	W	WA	A	A	A	Wh	AN	A
Sn ⁴⁺	W	(A)	(A)	W	W	W	W	W	A	W	A	A	W	(A)	W	WA	A	A	A	W	N	A
Co	W	(A)	(A)	W	W	W	W	W	A	W	I	N	W	(A)	W	W	A	A	A	W	(A)	W
Ni	W	(A)	(A)	W	W	W	W	W	A	W	I	N	W	(A)	W	W	A	A	A	W	(A)	W
Fe ²⁺	W	(A)	(A)	W	W	W	W	W	A	W	I	N	W	(A)	W	W	A	A	A	W	(A)	W
Fe ³⁺	W	(A)	(A)	W	W	W	W	W	A	W	I	N	W	(A)	W	W	A	A	A	W	(A)	W
Cr	W	(A)	(A)	W	W	W	W	W	A	W	I	N	W	(A)	W	W	A	A	A	W	AR	W
Al	W	(A)	(A)	W	W	W	W	W	A	W	I	N	W	(A)	W	W	A	A	A	W	A	W
Mn	W	(A)	(A)	W	W	W	W	W	A	W	I	N	W	(A)	W	W	A	A	A	W	A	W
Zn	W	(A)	(A)	W	W	W	W	W	A	W	I	N	W	(A)	W	W	A	A	A	W	(A)	W
Ba	W	(A)	(A)	W	W	W	W	W	A	W	I	N	W	(A)	W	W	A	A	A	W	(A)	W
Sc	W	(A)	(A)	W	W	W	W	W	A	W	I	N	W	(A)	W	W	A	A	A	W	(A)	W
Ca	W	(A)	(A)	W	W	W	W	W	A	W	I	N	W	(A)	W	W	A	A	A	W	(A)	W
Mg	W	(A)	(A)	W	W	W	W	W	A	W	I	N	W	(A)	W	W	A	A	A	W	(A)	W
NH ₄	W	(A)	(A)	W	W	W	W	W	A	W	I	N	W	(A)	W	W	A	A	A	W	(A)	W
Na	W	(A)	(A)	W	W	W	W	W	A	W	I	N	W	(A)	W	W	A	A	A	W	(A)	W
K	W	(A)	(A)	W	W	W	W	W	A	W	I	N	W	(A)	W	W	A	A	A	W	(A)	W
Li	W	(A)	(A)	W	W	W	W	W	A	W	I	N	W	(A)	W	W	A	A	A	W	(A)	W

W = Slightly soluble in water

W = Soluble in water

Wh = Soluble in hot water

W = Decomposed by water

A = Soluble in dilute acids

A = Soluble in concentrated acids

N = Soluble in certain ammonium compounds

I = Insoluble in water, acids or ammonium compounds

(A) = Gelatinous substances usually formed

(A) = Soluble in nitric acid, usually insoluble in hydrochloric acid

AR = Soluble in aqua regia

TABLE 7. SOLUBILITY OF COMMON SALTS

In Grams Per Liter at the Given Temperatures

	0°	50°	100°		0°	50°	100°
Ammonium alum .	26	159		Potassium dichromate	30	505(60°)	1020
Ammonium chloride	297	504	773	Potassium hydroxide	970	1400	1780
Ammonium nitrate	1183	3540	8710	Potassium iodide .	1279	1680	1780
Ammonium sulphate	706	844	1033	Potassium nitrate	133	855	2460
Barium chloride .	316	436	588	Potassium platinum chloride	7	22	52
Barium nitrate	50	171	342	Potassium sulphate	74	165	241
Borax .	16(10°)	105	523	Silver nitrate	1150	4000	9100
Calcium chloride	595	1250	1590	Sodium bromide	795	1160	1205
Cobalt chloride	405	935	*1030	Sodium carbonate (10 aq.)	71	409(30°)	
Copper nitrate	888	2078(80°)		Sodium carbonate (7 aq.)	204	475	452
Ferrous chloride	685(20°)	820	1060	Sodium chloride	356	387	391
Ferric chloride	744	3151	5357	Sodium hydroxide	420	1450	3130(80°)
Ferrous sulphate	156	486	430(90°)	Sodium iodide	1590	2280	3620
Lead nitrate	365	787	1270	Sodium nitrate	730	1140	1755
Magnesium chloride	528	575(40°)	730	Sodium phosphate	25	639(40°)	988
Magnesium sulphate (7 aq.) .	260	456(40°)		Sodium sulphate (10 aq.)	30	468	427
Magnesium sulphate (6 aq.)	408	504	738	Sodium sulphate (7 aq.)	196	468	427
Mercuric chloride	43	113	540	Sodium sulphate	141	495(40°)	336
Nickel chloride	600(10°)	760		Sodium thiosulphate	525	1697	2660
Nickel sulphate	272	502	776	Strontium chloride	442	744	1019
Potassium bromide.	540	860(60°)	1050	Strontium nitrate	395	926	1011
Potassium carbonate	1050	1210	1560	Zinc nitrate .	2948	2069(40°)	.
Potassium chloride	285	429	566	Zinc sulphate		768	785
Potassium chlorate	33	197	560				
Potassium chromate	589	690	791				

*Slow after 50°.

TABLE 8. SOLUBILITY OF GASES IN WATER

(Weight in Grams)

	0°	20°		0°	20°
Oxygen O ₂ . . .	0705	0443	Carbon dioxide CO ₂	3 35	1 69
Hydrogen H ₂ . . .	00192	00160	Hydrogen sulphide H ₂ S	7 10	3 98
Nitrogen N ₂ . . .	0293	0189	Ammonia NH ₃	987 000	535 00
Bromine Br ₂ . . .	431 000	148 000	Sulphur dioxide SO ₂	228 00	113 00
Chlorine Cl ₂ . . .		7 29			

TABLE 9. CRITICAL TEMPERATURE AND PRESSURE
OF GASES

Substance	Critical Temperature C°	Critical Pressure in Atmospheres	Substance	Critical Temperature C°	Critical Pressure in Atmospheres
Air .	-140	39	Ethylene	9 9	51 1
Alcohol	243 6	62 76	Fluorine	-121 0	50 6
Alcohol, methyl	239 95	78 5	Helium	< -268	. .
Ammonia .	130	15	Hydrogen	-240 8	14
Argon .	-117 4	52 9	Hydrogen chloride	51 25	86 0
Bromine	302 2		Methane	-81 8	54 9
Carbon dioxide	31 2	73	Nitrogen	-146 0	35 0
Carbon monoxide	-141 1	35 9	Nitrogen dioxide	-93 5	71 2
Carbon disulphide	277 7	78 1	Nitrogen monoxide N ₂ O	35 4	75
Chloroform .	260	54 9	Oxygen	-118	50
Chlorine	141 0	83 9	Sewer gas	100	88 7
Ethane	32 1	49	Sulphur dioxide	155 4	78 9
Ether. ...	194 4	35 61	Water	374	217 5

TABLE 10. RELATIVE HARDNESS OF ELEMENTS

Carbon (Diamond)	10	Copper	.3 0	Tin	. . .1.8
Boron	9.5	Antimony	3 0	Strontium.	1 8
Chromium . . .	9	Aluminum	2 9	Calcium1.5
Osmium.	7	Silver . . .	2.7	Gallium.1.5
Silicon.	7	Bismuth . . .	2 5	Lead1.5
Iridium.	6.5	Zinc . . .	2 5	Indium1.2
Ruthenium. . . .	6.5	Gold . . .	2 5	Lithium	0 6
Manganese. . .	5	Tellurium. . .	2 3	Phosphorus . . .	0 5
Palladium. . . .	4 8	Cadmium . .	2 0	Potassium. . . .	0.5
Iron.	4.5	Sulphur . . .	2 0	Sodium	0.4
Platinum	4.3	Selenium . . .	2.0	Rubidium.	0 3
Arsenic.	3.5	Magnesium. .	2.0	Caesium.	0.2

TABLE 11. HARDNESS OF SOLIDS OTHER THAN ELEMENTS

(Alphabetical Arrangement)

Agate ...	7	Fluorite	4	Opal . .	4-6
Alum. . .	2-2 5	Galena	2 5	Phosphorbronze .	4
Amber.	2-2 5	Garnet	7	Platinum-Iridium	6 5
Anthracite	2 2	Glass	4 5-6 5	Pyrite .	6 3
Asbestos	5	Graphite	0 5-1	Quartz .	7
Asphalt ...	1-2	Gypsum	1 6-2	Rock salt .	2
Bell metal	4	Hematite	6	Silver chloride .	1 3
Boric acid	3	Kaolin	1	Steel .	5-8 5
Brass. .	3-4	Loess ..	0 3	Talcum .	1
Corundum	9	Magnetite	6	Topaz .	8
Dolomite	3 5-4	Marble ..	3-4	Wax. . .	0 2
Feldspar . .	6	Mica	2 8	Wood's metal .	.3
Flint.7				

TABLE 12. MOHS'S SCALE OF HARDNESS SHOWING CHIEF CONSTITUENT OF EACH MEMBER

1. Talc (Soapstone) MgSiO_3	6 Feldspar KAlSi_3O_8
2. Gypsum CaSO_4	7 Quartz SiO_2
3. Calcite CaCO_3	8. Topaz Al_2O_3 or Beryl $\text{Al}_2\text{Ge}_3(\text{SiO}_3)_6$
4. Fluorspar CaF_2	9 Corundum Al_2O_3
5. Apatite $\text{Ca}_5(\text{PO}_4)_3 + \text{CaF}_2$ or CaCl_2	10. Diamond C

TABLE 13. SPECIFIC GRAVITY OF ELEMENTS

Under Varying Conditions

Aluminum	Cast	2 56-2 58	Lithium		0 534
	Wrought	2 65-2 8	Magnesium		1 741
	Pure	2 58	Manganese		7 42
Antimony	Amorphous	6 22	Mercury	Liquid	13 596 (0°)
	Compressed	6 691		Liquid	13 546 (20°)
Argon		1 3845-1 4233		Liquid	13 690 (-38 8°)
Arsenic	Crystallized	5 73		Solid	14 193 (-38 8°)
	Amorphous	3 70		Solid	14 383 (-188°)
Barium	Solid	3 78	Molybdenum		9 01
Bismuth	Solid	9 70-9 90	Neodymium		6 96
	Liquid	10	Nickel	Solid	8 60-8 90
Boron	Crystallized	2 535	Phosphorus	Red	2 20
	Amorphous	2 45		Yellow	1 83
Bromine	Liquid	3 12		Metallic	2 34
Cadmium	Cast	8 54-8 57	Platinum		21 37 (20°)
	Wrought	8 67	Potassium		.87 (20°)
	Solid	8 37 (318°)		Solid	.851 (62 1°)
	Liquid	7 99 (318°)		Liquid	.830 (62 1°)
Caesium		1 873	Silicon	Crystallized	2 42
Calcium		1 85		Amorphous	2 35
Carbon	Diamond	3 52	Silver	Cast	10 42-10 53
	Graphite	2 25		Wrought	10 6
Chlorine	Liquid	1 507 (-33 6°)		Liquid	9 51
Chromium	Pure	6 92 (20°)	Sodium		9712 (20°)
Cobalt		8 4 (15°)		Solid	9519 (97 6°)
Copper	Liquid	8 217		Liquid	9287 (97 6°)
	Solid	8 30-8 95	Strontium		2 50-2 58
Gold	Cast	19 3	Sulphur		2 0-2 1
	Wrought	19 33		Liquid	1 811
Helium	Liquid	0 15 (-269°)	Tin	White cast	7 29
Hydrogen	Liquid	0 070 (-252°)		White wrought	7 30
Iridium		22 42 (17°)		White crystallized	6 97-7 18
Iodine	Solid	4 940 (20°)		Whitesolid	7 184 (226°)
Iron	Pure	7 85-7 88		Whiteliquid	6 99 (226°)
	Gray cast	7 03-7 13		Gray	5 8
	White cast	7 58-7 73	Tungsten		18 6-19 1
	Wrought	7 80-7 90	Vanadium		5 69
	Liquid	6 85	Zinc	Cast	7 04-7 16
	Steel	7 60-7 80		Wrought	7 19
Lead	Cast	11 37		Liquid	6 48
	Wrought	11 36			
	Solid	11 005 (325°)			
	Liquid	10 645 (325°)			

TABLE 14. SPECIFIC GRAVITY OF SOLIDS OTHER THAN ELEMENTS

Agate	2.5-2.7	Fluorite	3.18	Meerschaum	0.99-1.28
Amber	1.06-1.11	Garnet	3.15-4.3	Mica	2.6-3.2
Anthracite	1.4-1.8	Gas carbon	1.88	Olivine	3.27-3.37
Asbestos	2.0-2.8	Gelatin	1.27	Opal	2.2
Asphalt	1.1-1.5	Glass	2.4-2.8	Orthoclase	2.58-2.61
Basalt	2.4-3.1	Glass, flint	2.9-5.9	Paper	0.7-1.15
Beeswax	0.96-0.97	Glue	1.27	Peat	0.84
Bone	1.7-2.0	Granite	2.64-2.76	Pitch	1.07
Brick	1.4-2.2	Graphite	2.30-2.72	Porcelain	2.3-2.5
Butter	0.88-0.87	Gum arabic	1.3-1.4	Pyrite	4.95-5.1
Celluloid	1.4	Gypsum	2.31-2.33	Quartz	2.65
Cement	2.7-3.0	Hematite	4.9-5.3	Resin	1.07
Chalk	1.9-2.8	Ice	0.917	Rock salt	2.18
Charcoal (oak)	0.57	Ivory	1.83-1.92	Rubber	0.92-0.99
Charcoal (pine)	0.28-0.44	Lava	2.0-3.0	Sandstone	2.14-2.36
Chrome yellow	6.0	Leather (dry)	0.86	Slag (furnace)	2.0-3.9
Cinnabar	8.12	Leather (greased)	1.02	Slate	2.6-3.3
Clay	1.8-2.6	Lime (mortar)	1.65-1.78	Soapstone	2.6-2.8
Coal (soft)	1.2-1.5	Lime (slaked)	1.3-1.4	Starch	1.53
Coke	1.0-1.7	Limestone	2.68-2.76	Sugar	1.61
Corundum	3.9-4.0	Litharge (artificial)	9.3-9.4	Talcum	2.7-2.8
Diamond	3.51-3.55	Litharge (natural)	7.8-8.0	Tallow	0.91-0.97
Emery	4.0	Magnetite	4.9-5.2	Topaz	3.5-3.6
Feldspar	2.55-2.75	Marble	2.6-2.84	Tourmaline	3.0-3.2
Flint	2.63				

TABLE 15 SPECIFIC GRAVITY OF LIQUIDS

Fluid	Sp. Gr.	Temp.	Fluid	Sp. Gr.	Temp.
Acetone	0.792	20°	Naphtha (wood)	0.848-0.810	0°
Alcohol (ethyl)	0.807	0°	Naphtha (petroleum ether)	0.665	15°
Alcohol (methyl)	0.810	0°	Oils		
Aniline	1.035	0°	Castor	0.969	15°
Benzol	0.899	0°	Cocoonut	0.925	15°
Bromine	3.187	0°	Lard	0.920	15°
Carbon disulphide	1.293	0°	Lemon	0.844	16°
Chloroform	1.526	18°	Linseed (boiled)	0.942	15°
Carbolic acid	0.950-0.965	15°	Olive	0.918	15°
Ether	736	0°	Turpentine	0.873	16°
Gasoline	0.66-0.69	15°	Petroleum	0.878	0°
Glycerine	1.260	0°	Petroleum (light)	0.795-0.805	15°
Milk	1.029-1.033	15°	Water	1	4°

TABLE 16. SPECIFIC GRAVITY AND WEIGHT OF GASES

<i>Name of Gas</i>	<i>Formula</i>	<i>Specific Gravity</i>	<i>Weight of 1 liter in Grams</i>
Air		1 000	1 2928
Acetylene	C_2H_2	0 92	1 1620
Ammonia	NH_3	0 597	0 7706
Argon	A	1 379	1 782
Benzene	C_6H_6	2 69463	3 485
Bromine	Br	5 524	7 1388
Carbon dioxide	CO_2	1 5291	1 9768
Carbon monoxide	CO	0 9672	1 2506
Chlorine	Cl_2	2 491	3 1674
Coal gas	0 320-0 740	0 414-0 957
Cyanogen	C_2N_2	1 806	2 3229
Ethane	C_2H_6	1 0494	1 3567
Ethylene	C_2H_4	0 96749	1 251
Fluorine	F_2	1 26	1 697
Helium	He	1 368	0 1787
Hydrofluoric acid	HF	0 7126	0 894
Hydrobromic acid	HBr	2 71	3 6163
Hydrochloric acid	HCl	1 2684	1 6398
Hydrogen	H_2	0 06925	0 08984
Hydrogen sulphide	H_2S	1 1895	1 5230
Methane	CH_4	0 5576	0 7160
Neon	Ne	0 6963	0 9002
Nitrogen	N_2	0 9673	1 2514
Nitrogen dioxide	N_2O_2	1 0367	1 3402
Nitrogen monoxide	N_2O	1 5298	1 9777
Nitrogen tetroxide	N_2O_4	1 5878	2 053
Oxygen	O_2	1 053	1 4292
Sulphur dioxide	SO_2	2 2639	2 9266
Steam at 100°	H_2O	0 469	0 581
Water gas	0 53883	0 697

TABLE 17. MELTING POINT AND SPECIFIC HEAT OF ELEMENTS

<i>Elements</i>	<i>Melting Point</i>	<i>Specific Heat</i>	<i>Elements</i>	<i>Melting Point</i>	<i>Specific Heat</i>
Aluminum	658 ± 1	0 225	Mercury	-38 7	{ 0 0319 s 0 033 1
Antimony	630 ± 1	0 0508	Molybdenum	2535	
Argon	-188		Neodymium	840	
Arsenic	500	0 0822	Neon	-252	
Barium	850		Nickel	1452	0 018
Beryllium	< Ag		Niobium	1950	
Bismuth	264	0 0308	Nitrogen	-211	
Boron	>2000 < 2500	0 5	Osmium	ab 2700	
Bromine	-7 3		Oxygen	-227 \pm 3	
Cadmium	321	0567	Palladium	1545 \pm 15	
Caesium	26		Phosphorus	44 2	0 202
Calcium	805		Platinum	1755 \pm 20	0 0324
Carbon	>3500		Potassium	62 3	0 166
Cerium	645		Praseodymium	940	
Chlorine	-102		Rhodium	1910	
Chromium	>1520		Rubidium	38 5	
Cobalt	1478	0 107	Silicon	1420	
Copper	1083 \pm 3	0 095	Silver	961 \pm 1	0 057
Fluorine	-223		Sodium	97	0 2934
Gallium	30 1		Sulphur	113 5-119 5	0 178
Gold	1063 \pm 3	0 0324	Tantalum	2800	
Hydrogen	-260 \pm 1		Tellurium	451	
Indium	155		Thorium	>1700 < Pt	
Iodine	114	0 0541	Tin	231 9 \pm 2	0 056
Iridium	2290		Titanium	1795	
Iron	1530	0 114	Tungsten	2950	
Krypton	-169		Vanadium	1720	
Lanthanum	810		Xenon	-140	
Lead	327 \pm 0 5	0 0314	Zinc	419 \pm 0 5	0 0956
Lithium	186		Zirconium	>8	
Magnesium	651	0 250			
Manganese	1260	0 122			

TABLE 18. MELTING POINT OF INORGANIC COMPOUNDS

<i>Substance</i>	<i>Formula</i>	<i>Specific Gravity 20°</i>	<i>Melts C°</i>
Aluminum chloride	AlCl_3		190
Aluminum nitrate..	$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$		72.8
Aluminum oxide .	Al_2O_3 . . .	4 00	2020
Ammonia.	NH_3 .	.	-75
Ammonium nitrate ..	NH_4NO_3 .	1 72	165
Ammonium sulphate	$(\text{NH}_4)_2\text{SO}_4$.	1 77	140
Antimony chloride	SbCl_3 .	3 06	73
Arsenic chloride	AsCl_3 .	2 20	-18
Barium chloride .	$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	3 10	113
Bismuth chloride .	BiCl_3	4 56	232.5
Boric acid.	H_3BO_3	1 46	185
Boric anhydride	B_2O_3 . . .	1 79	577
Borax	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	1 69	561 +
Cadmium chloride	CdCl_2 .	4 05	560
Cadmium nitrate.	$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	2 45	59.5
Calcium chloride ..	CaCl_2 . . .	2 26	774
Calcium chloride	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	1 68	29.6
Calcium nitrate . . .	$\text{Ca}(\text{NO}_3)_2$..	2 36	499
Calcium nitrate.	$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	1 82	42 3
Chromium nitrate .	$\text{Cr}(\text{NO}_3)_3$	37
Copper chloride... .	CuCl_2 . . .	3 05	498
Copper chloride	CuCl .	3 7	431
Copper nitrate... .	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	2 05	114.5
Ferric chloride... .	FeCl_3 . . .	2 80	301
Ferric nitrate.	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$.	1 68	47 2
Ferrous sulphate... .	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$.	1 90	64
Lead chloride.	PbCl_2 . . .	5 8	500
Magnesium chloride .	MgCl_2	2 18	708
Magnesium nitrate ...	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	1 46	90
Magnesium sulphate . .	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	1 68	150
Manganese chloride . .	$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$.	2 01	87 5
Manganese nitrate . .	$\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	1 82	26
Manganese sulphate. . .	$\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$	2 09	54
Mercurous chloride. . .	HgCl .	7 10	450 ±
Mercuric chloride....	HgCl_2 .	5 40	288
Nickel nitrate	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	2 05	56 7
Nickel sulphate . . .	$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	1 98	99

Table 18 (Continued)

<i>Substance</i>	<i>Formula</i>	<i>Specific Gravity 20°</i>	<i>Melts C°</i>
Potassium carbonate . .	K_2CO_3	2 29	840 ±
Potassium chlorate . . .	$KClO_3$	2 34	372
Potassium chromate . . .	K_2CrO_4	2 72	975
Potassium cyanide	KCN	1 52	
Potassium chloride	KCl	1 99	801
Potassium nitrate	KNO_3	2 10	341
Potassium perchlorate . .	$KClO_4$	2 52	610
Potassium phosphate . .	KH_2PO_4	2.34	96
Potassium acid sulphate .	$KHSO_4$	2.35	205
Silver chloride	$AgCl$	5 56	460
Silver nitrate	$AgNO_3$	4 35	208 7
Silver sulphate	Ag_2SO_4	5 45	655 ±
Sodium chloride	$NaCl$	2 17	800
Sodium hydroxide	$NaOH$	2 1	318
Sodium nitrate	$NaNO_3$	2 26	315
Sodium chlorate	$NaClO_3$	2 48	248
Sodium carbonate	Na_2CO_3	2 48	852
Sodium carbonate	$Na_2CO_3 \cdot 10H_2O$	1 46	34
Sodium phosphate	$Na_2HPO_4 \cdot 12H_2O$	1 54	38
Sodium sulphate	$Na_2SO_4 \cdot 10H_2O$	1.46	32 38
Sodium thiosulphate	$Na_2S_2O_3 \cdot 5H_2O$	1 73	48 16
Stannous chloride	$SnCl_2$	250
Zinc chloride	$ZnCl_2$	2.91	365
Zinc chloride	$ZnCl_2 \cdot 3H_2O$	6 5
Zinc nitrate	$Zn(NO_3)_2 \cdot 6H_2O$	2 06	36 4
Zinc sulphate	$ZnSO_4 \cdot 7H_2O$	2 02	50

TABLE 19. TENSILE STRENGTH

(lb. per sq. in.)

Aluminum (wire)	30,000– 40,000
Brass (wire)	50,000–150,000
Bronze, phosphorus (hard drawn)	110,000–140,000
Bronze, silica (hard drawn)	95,000–115,000
Bronze	60,000– 75,000
Copper (wire, hard drawn)	60,000– 70,000
Gold	20,000
Iron (cast)	13,000– 33,000

Table 19 (Continued)

Iron (wire, hard drawn)	80,000-120,000
“ (annealed)	50,000- 60,000
Lead (cast or drawn)	2,600- 3,300
Platinum.	50,000
Silver ..	42,000
Steel	80,000-330,000
“ (maximum strength)	460,000
“ piano wire, .033 in. diameter	357,000-390,000
“ “ “ .051 “ “	325,000-337,000
Tin (cast or drawn)	4,000- 5,000
Zinc (cast)	7,000- 13,000
Zinc (drawn)	22,000- 30,000

TABLE 20. FUSIBLE METALS

The figures under each metal show the percentage required to make an alloy that melts at the temperature expressed in the left hand column

<i>Melting Point</i>	ALLOY CONTAINS			
	<i>Cadmium</i>	<i>Tin</i>	<i>Lead</i>	<i>Bismuth</i>
65 5	10.8	14 2	24.9	50 1
67 5	10 2	14 3	25 1	50.4
68.5	14.8	7 0	26 0	52 2
68.5	13.1	13 8	24.3	48 8
75.5	6.2	9 4	34 4	50 0
89.5	7 1	0	39 7	53.2
95	6.7	0	43 4	49 9
96	0	15 5	32 0	52 5
101	0	19 8	25 8	54 4
125	0	15 0	25.0	60 0
128	0	14.0	43.0	43 0
145	0	33 3	33 3	33.3
148	0	23 1	10.7	66 2
161	0	33.0	50 0	17 0
181	0	52 1	35.8	12 1
182	0	60.0	20 0	20 0
234	0	9 1	70.9	20 0

TABLE 21. FREEZING MIXTURES

	<i>Parts by Weight</i>		<i>Parts by Weight</i>	<i>Temper- ature Produced</i>
Sodium acetate	85	Water	100	-4 7
Ammonium chloride	30	Water	100	-5.1
Calcium chloride	250	Water	100	-12 4
Sodium chloride	33	Snow	100	-21.3
Calcium chloride	30	Snow	100	-10.9
Ammonium chloride	25	Snow	100	-15 4
Sulphuric acid and water (66 1% acid)	1	Snow	13 08	-16
Sulphuric acid and water (66 1% acid)	1	Snow	4 32	-25
Sulphuric acid and water (66 1% acid)	1	Snow	1 097	-37
Alcohol at 4°	77	Snow	73	-30
Alcohol	..	Solid carbon dioxide		-72
Chloroform	.	Solid carbon dioxide		-77
Ether	Solid carbon dioxide		-77
Liquid sulphur dioxide		Solid carbon dioxide		-82

TABLE 22. HEAT OF COMBUSTION OF FUELS, ETC.

<i>Substance</i>	<i>Formula</i>	<i>Products of Combustion</i>	<i>Calories per gram</i>	<i>B. T. U. per pound</i>
Acetylene . . .	C_2H_2	CO_2, H_2O	11923	21461
Ammonia . . .	NH_3	N, H_2O	5332	
Alcohol, amyl	$C_5H_{11}OH$	CO_2, H_2O	8985	16173
“ denatured ethyl		CO_2, H_2O	6455	11619
“ ethyl . . .	C_2H_5OH	CO_2, H_2O	7183	12929
“ methyl . . .	CH_3OH	CO_2, H_2O	5307	9552
Benzene	C_6H_6	CO_2, H_2O	9977	17958
Carbon disulphide	CS_2	CO_2, SO_2	3244	5839
Carbon monoxide	CO	CO_2	2442	4395
Coal, sub-bituminous, poor.		CO_2, H_2O	5115	9207
“ “ good..		CO_2, H_2O	5865	10557
“ bituminous, poor . . .		CO_2, H_2O	6088	10958
“ “ good		CO_2, H_2O	7852	14134
“ semi-bituminous, poor		CO_2, H_2O	7845	14121
“ “ good		CO_2, H_2O	8166	14699
“ semi-anthracite		CO_2, H_2O	7612	13702
“ anthracite, poor. . .		CO_2, H_2O	6987	12577
“ “ good . . .		CO_2, H_2O	7417	13351
Coal tar		CO_2, H_2O	8667	15600
Coke		CO_2, H_2O	7000	12600
Ethane	C_2H_6	CO_2, H_2O	12347	22220
Ethylene	C_2H_4	CO_2, H_2O	11884	21391
Gas, coal		CO_2, H_2O	11000	19800
Gas, water		CO_2, H_2O	5500	9900
Gasoline		CO_2, H_2O	11250	20250
Hydrogen	H_2	H_2O	34218	61592
Hydrogen sulphide	H_2S	H_2O, SO_2	3488	6278
Kerosene		CO_2, H_2O	11100	19980
Methane	CH_4	CO_2, H_2O	13244	23839
Naphthalene	$C_{10}H_8$	CO_2, H_2O	9619	17314
Oil, lard		CO_2, H_2O	9400	16920
“ olive		CO_2, H_2O	9442	17656
“ petroleum, heavy		CO_2, H_2O	10350	18630
Propylene	C_3H_6	CO_2, H_2O	11731	21116
Wood, Beech (12.9% H_2O).		CO_2, H_2O	4168	7502
“ Birch (11.83% H_2O)		CO_2, H_2O	4207	7572
“ Oak (13.3% H_2O) . .		CO_2, H_2O	3990	7182
“ Pine (12.17% H_2O) . .		CO_2, H_2O	4422	7959

**TABLE 23. BRIGHTNESS OF VARIOUS LIGHT SOURCES IN
CANDLE POWER, PER SQUARE INCH OF SURFACE OF
LIGHT ACCORDING TO THE NATIONAL ELECTRIC
LIGHT ASSOCIATION**

Sun at zenith	600,000
Crater carbon arc	200,000
Open carbon arc	10,000-50,000
Flaming arc	5,000
Nernst glower (1.5 w. p. c.)	2,200
Tungsten incandescent (1 1/2 w. p. c.)	1,000
Tungsten incandescent (1.25 w. p. c.)	875
Tantalum incandescent (2. w. p. c.)	750
Graphitized carbon filament (2.5 w. p. c.)	625
Carbon incandescent (3 1/2 w. p. c.)	480
Carbon incandescent (3.5 w. p. c.)	375
Inclosed carbon arc d. c.	100-500
Inclosed carbon arc a. c.	75-200
Acetylene flame (1 foot burner)	75-100
Welsbach Mantle	20-50
Cooper Hewitt mercuric vapor lamp	17
Kerosene flame.	3-8
Candle flame	3-4
Gas flame (fish tail)	3-8
Frosted incandescent bulb	2-5

TABLE 24. ORGANIC COMPOUNDS

Substance	Formula	Specific Gravity	At Temp C.	Melts C.°	Boils C.°
Acetic acid	CH_3COOH	1 115	0	16 7	118 5
Acetone . .	CH_3COCH_3	0 812	0	-94 6	56 1
Aldehyde . .	$\text{C}_2\text{H}_4\text{O}$	0 806	0	-120	20 8
Aniline.	$\text{C}_6\text{H}_5\text{NH}_2$	1 038	0	-8	183 9
Beeswax . .		0 96 \pm		62	
Benzoic acid	$\text{C}_6\text{H}_5\text{O}_2$	1 293	4	121	249
Benzol	C_6H_6	0 879	20	5 58	80 2
Butter . .		86-7		30 \pm	
Camphor	$\text{C}_{10}\text{H}_{16}\text{O}$	0 99	10	176	209
Carbolic acid	$\text{C}_6\text{H}_5\text{OH}$	1 060	21	43	182
Carbon disulphide	CS_2	1 292	0	-110	46 2
Carbon tetrachloride	CCl_4	1 582	21	-30	76 7
Chloroform	CHCl_3	1 526	0	-65	61 2
Ethyl chloride	$\text{C}_2\text{H}_5\text{Cl}$	0 918	8	-141 6	14
Ethyl ether	$(\text{C}_2\text{H}_5)_2\text{O}$	0 736	0	-118	34 6
Formic acid	HCOOH	1 242	0	86	100 8
Gasoline . .		0 68 \pm			70-90
Glycerin . .	$\text{C}_3\text{H}_8(\text{OH})_3$	1 269	0	20	290
Iodoform	CHI_3	2 25	25	119	
Lard				38 \pm	
Naphthalene	C_{10}H_8	1 152	15	80	218
Nitrobenzol .	$\text{C}_6\text{H}_5\text{NO}_2$	1 212	7 5	5	211
Nitro-glycerine	$\text{C}_3\text{H}_5(\text{NO}_2)_3$	1 60			
Olive oil . . .		918			300 \pm
Oxalic acid . . .	$\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	1 68		190	
Paraffin wax (soft)		90 \pm		38-52	350-390
Paraffin wax (hard)				52-56	390-430
Spermacetti				45 \pm	
Starch	$(\text{C}_6\text{H}_{10}\text{O}_5)_x$	1 56			
Sugar, cane.	$\text{C}_{12}\text{H}_{22}\text{O}_{11}$	1 588	20		160
Stearin	$\text{C}_{18}\text{H}_{36}(\text{C}_{17}\text{H}_{33}\text{O}_2)$	0 925	65		
Tartaric acid	$\text{H}_2\text{C}_4\text{H}_4\text{O}_6$	1 754			
Tallow, beef				40-45	
Tallow, mutton				44-45	
Toluene	$\text{C}_6\text{H}_5\text{CH}_3$	0 882	20	-92	111

TABLE 25. COMPARISON OF METALLIC ELEMENTS AND COMPOUNDS

<i>Metal</i>	<i>Chief Natural Compound</i>	<i>Method Prepared by</i>	<i>Chief Commercial Compound</i>	<i>Other Important Compounds</i>	<i>Common Color of Salts</i>
Aluminum	Al ₂ O ₃ , 2H ₂ O	Electrolysis	AlCl ₃	Al ₂ (SO ₄), 18H ₂ O; Al(OH) ₃	White
Ammonium	—	Not known	NH ₄ Cl	NH ₄ NO ₃ , (NH ₄) ₂ SO ₄	White
Bismuth	Bi ₂ S ₃ ; Bi ₂ O ₃	Roasting, Electrolysis	Bi(OH) ₃ NO ₃ , BiONO ₃	BiCl ₃	White
Antimony	Sb ₂ S ₃	Heating with iron	SbCl ₃	Sb ₂ S ₃ ; Sb ₂ O ₃	Colorless to red-orange
Calcium	CaCO ₃ , CaSO ₄ , 2H ₂ O	Electrolysis	CaCO ₃	CaO, (CaSO ₄), H ₂ O, Ca(OH) ₂	Colorless or white
Chromium	FeCr ₂ O ₄	Electrolysis; Thermit	PbCrO ₄	K ₂ Cr ₂ O ₇ ; K ₂ Cr ₂ O ₇	Green, yellow to red
Cobalt	CoAsS	Chemical methods	Potassium cobalt silicate	CoCl ₂ , 6H ₂ O; Co(NO ₃), 6H ₂ O	Pale red
Copper	Cu ₂ O; CuS; CuFeS ₂ ; native	Furnace	CuSO ₄ , 5H ₂ O	CuCO ₃ , Cu(OH) ₂ ; CuCl ₂ , 2H ₂ O; Cu(NO ₃) ₂ , 3H ₂ O	Blue, greenish
Gold	Au ₂ Te ₂ , native	Amalgamation	AuCl ₃ , HCl, 4H ₂ O	KAu(CN) ₂	Yellow
Iron	Fe ₂ O ₃ ; Fe ₃ O ₄	Furnace	FeSO ₄ , 7H ₂ O; FeCl ₃ , 6H ₂ O	FeS, (NH ₄) ₂ HF ₆ (C ₄ H ₉ O ₂), K ₂ Fe(CN) ₆ , 3H ₂ O	Greenish (ous); red-brown (ic)
Lead	PbS	Furnace	2PbCO ₃ , Pb(OH) ₂	Pb(C ₂ H ₃ O ₂), 3H ₂ O; Pb ₃ O ₄ , PbS	White
Magnesium	MgCO ₃ ; KCl, MgCl ₂	Electrolysis	MgSO ₄ , 7H ₂ O	MgCO ₃ , MgO, MgCl ₂ , 6H ₂ O	White
Manganese	MnO ₂	Furnace, Thermit	MnO ₂	MnCl ₂ , 4H ₂ O; KMnO ₄	Pink, purple
Mercury	HgS; native	Furnace	HgCl ₂ , HgCl	HgO, HgS, HgI ₂ , HgNO ₃ , 2H ₂ O	White
Nickel	NiS, NiAs	Furnace	NiSO ₄ , 7H ₂ O	Ni(NH ₄)(SO ₄), 6H ₂ O, NiCl ₂ , 6H ₂ O, Ni(NO ₃), 6H ₂ O	Green
Platinum	PlAs ₂ , native	Chemical methods	H ₂ POCl ₄ , 6H ₂ O	(NH ₄) ₂ P ₂ Cl ₆ , K ₂ P ₂ Cl ₆	Brownish-red
Potassium	KCl, K ₂ SO ₄	Electrolysis	K ₂ SO ₄ , KOH; KNO ₃	KCN, K ₂ CO ₃ , KClO ₄ , KCl	White
Silver	Ag ₂ S, AgCl; native	Amalgamation, chemical	AgNO ₃	KAg(CN) ₂ ; AgBr, AgCl	White
Sodium	NaCl, NaNO ₃	Electrolysis	NaCl	NaHCO ₃ , Na ₂ CO ₃ , 10H ₂ O, NaOH, Na ₂ SO ₄ , 10H ₂ O	White, colorless
Tin	SnO ₂	Furnace	SnCl ₂ , 2H ₂ O	SnCl ₄	White
Zinc	ZnS; ZnO, ZnCO ₃	Furnace	ZnO	ZnCl ₂ ; ZnSO ₄ , 7H ₂ O, ZnS	White

TABLE 26. INTERNATIONAL ATOMIC WEIGHTS

<i>Element</i>	<i>Symbol</i>	<i>Atomic Weight</i>	<i>Common Valence</i>	<i>Element</i>	<i>Symbol</i>	<i>Atomic Weight</i>	<i>Common Valence</i>
Aluminum	Al	27 1	3	Molybdenum .	Mo	96 0	4, 6
Antimony	Sb	120 2	3, 5	Neodymium	Nd	144 3	3
Argon	A	39 9	0	Neon	Ne	20 2	0
Arsenic.	As	74 96	3, 5	Nickel	Ni	58 68	2, 3
Barium	Ba	137 37	2	Nitron	Nt	222	-
Bismuth	Bi	208 0	3, 5	Nitrogen	N	14 008	3, 5
Boron	B	10 9	3	Osmium	Os	190 9	6, 8
Bromine	Br	79 92	1	Oxygen	O	16 00	2
Cadmium	Cd	112 40	2	Palladium .	Pd	106 7	2, 4
Caesium	Cs	132 81	1	Phosphorus	P	31 04	3, 5
Calcium	Ca	40 07	2	Platinum .	Pt	195 2	2, 4
Carbon	C	12 005	4	Potassium	K	39 10	1
Cerium	Ce	140 25	3, 4	Praseodymium	Pr	140 9	3
Chlorine	Cl	35 46	1	Radium	Ra	226 0	2
Chromium	Cr	52 0	2, 3, 6	Rhodium	Rh	102 9	3
Cobalt .	Co	58 97	2	Rubidium	Rb	85 45	1
Columbium	Cb	93 1	1	Ruthenium	Ru	101 7	6, 8
Copper	Cu	63 57	1 2	Samarium	Sa	150 4	3
Dysprosium	Dy	162 5	3	Scandium	Sc	45 1	3
Erbium	Er	167 7	3	Selenium	Se	79 2	2, 4, 6
Europium .	Eu	152 0	3	Silicon	Si	28 3	4
Fluorine	F	19 0	1	Silver	Ag	107 88	1
Gadolinium	Gd	157 3	3	Sodium	Na	23 00	1
Gallium	Ga	70 1	3	Strontium	Sr	87 63	2
Germanium	Ge	72 5	4	Sulphur	S	32 06	2, 4, 6
Glucium	Gl	9 1	2	Tantalum	Ta	181 5	5
Gold	Au	197 2	1, 3	Tellurium	Te	127 5	2, 4, 6
Helium	He	4 00	0	Terbium	Tb	159 2	3
Holmium	Ho	163 5	3	Thallium	Tl	204 0	1, 3
Hydrogen	H	1 008	1	Thorium	Th	232 15	4
Indium	In	114 8	3	Thulium	Tm	169 9	3
Iodine	I	126 92	1	Tin .	Sn	118 7	2, 4
Iridium	Ir	193 1	4	Titanium	Ti	48 1	2, 3, 4
Iron .	Fe	55 84	2, 3	Tungsten	W	184 0	6
Krypton	Kr	82 92	0	Uranium	U	238 2	4, 6
Lanthanum	La	139 0	3	Vanadium	V	51 0	3, 5
Lead	Pb	207 20	2, 4	Xenon	Xe	130 2	0
Lithium .	Li	6 94	1	Ytterbium (Neo)	Yb	173 5	3
Lutecium	Lu	175 0	3	Yttrium	Yt	89 33	3
Magnesium	Mg	24 32	2	Zinc .	Zn	65 37	2
Manganese	Mn	54 93	2, 3, 4, 6, 7	Zirconium	Zr	90 6	4
Mercury	Hg	200 6	1, 2				

INDEX

References are to sections except where otherwise indicated, as app. 20, which means Table 20 in the appendix.

- Absolute scale of temperature, 32, 83
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